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INTRODUCTORY LECTURES ON THE PROPERTIES, DETECTION, AND CHEMICAL EFFECTS OF HIGH ENERGY RADIATIONS

DONALD J. METZ

September 1962

BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.
under contract with the
UNITED STATES ATOMIC ENERGY COMMISSION

UNIVERSITY OF MICHIGAN
3 9015 08658 2056

BNL 748 (T-274)
(Radiation Effects on Materials - TID-4500, 18th Ed.)

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UPTON, NEW YORK

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PRINTED IN USA
PRICE 75 CENTS

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D.C.

June 1963 900 copies

PREFACE

The following lectures were originally designed for presentation to Brazilian university students who attended the Atomic Energy Commission's Latin American "Atoms at Work" Exhibit, which was presented in Rio de Janeiro in May 1961. Subsequent considerations led to the conclusion that the lectures should be published in the present form. It is hoped that those who read these lectures will be stimulated to expand upon the material contained herein by making use of the references cited.

Part I

THE INTERACTION OF RADIATION WITH MATTER

INTRODUCTION

In preparation for a more detailed discussion of the effects of high energy radiations on specific types of materials, it is necessary to discuss the important general modes of interaction that are, to a certain extent, common to some types of radiations and some that are peculiarly specific for other types. During this preliminary phase of the discussion it should become apparent that the type of interaction depends not only on the particular nature of the radiation but also on its energy, and that frequently secondary interactions become important considerations.

Since the energies of the radiations under discussion are generally expressed in electron volts (or some larger multiple of this unit), it might be instructive to compare this unit with other energy units, with which the reader may be more familiar. The following relationships may be cited.

$$1 \frac{\text{electron volt}}{\text{particle}} \equiv 1.60 \times 10^{-12} \frac{\text{ergs}}{\text{particle}} \equiv 23{,}000 \frac{\text{calories}}{\text{mole}}.$$

Although the electron volt appears to be a rather small amount of energy when viewed on a per particle basis, it represents an appreciable amount of energy on a macroscopic basis, i.e., calories per mole. Another approach toward gaining an appreciation of the energy content implied by the electron volt is to express the average energy of a hydrogen molecule at standard temperature and pressure, moving at a speed of the order of 10^3 meters per second, in terms of electron volts. Such a particle would have a kinetic energy of ≈ 0.03 electron volts.

The various types of radiation may be conveniently categorized in the following fashion:

A. Charged particles
   1. Heavy particles – e.g., alpha particles, protons, and deuterons.
   2. Light particles – accelerated electrons and beta particles.

B. Uncharged particles – neutrons.

C. Electromagnetic radiation – x rays and gamma rays.

In the subsequent discussion the interactions between alpha particles and matter will be cursorily covered, mainly because of their important historical significance in the early development of radiation chemistry but also because of their similarity to the interactions between protons and matter. Interest in the latter is focused, not on direct proton irradiations, but on the fact that fast neutron irradiation of hydrogenous materials gives rise to internally produced proton irradiation. Next, the interactions with matter of accelerated electrons and beta particles will be discussed. A description will follow of the interactions of x rays and gamma rays with matter, both of which, as will be seen, give rise to internally generated secondary electron irradiation. Finally, the interactions with neutrons will be surveyed, with emphasis on irradiations performed within a nuclear reactor.

INTERACTIONS WITH ALPHA PARTICLES AND OTHER HEAVY CHARGED PARTICLES

An alpha particle is a doubly ionized helium nucleus, and therefore has an atomic mass number (A) of four and an atomic number or nuclear charge (Z) of two. Alpha particles of energies from 4 to 10 million electron volts (Mev) are emitted as the result of the decay of many naturally occurring or artificially produced radioactive nuclides. An alpha particle with an energy of 6 Mev will travel with a speed of $\approx 1.7 \times 10^9$ cm/sec ($\approx 6\%$ of the velocity of light in a vacuum) and has a range of ≈ 5 cm in air at standard temperature and pressure.

Because of its high charge (+2) and mass (4 mass units), an alpha particle interacts very strongly with matter which it traverses, compared with particles of smaller charge or smaller mass but the same energy.

The volume occupied by the positively charged nuclei of atoms is orders of magnitude smaller than that associated with their orbital electrons. When a positive particle, such as an alpha parti-

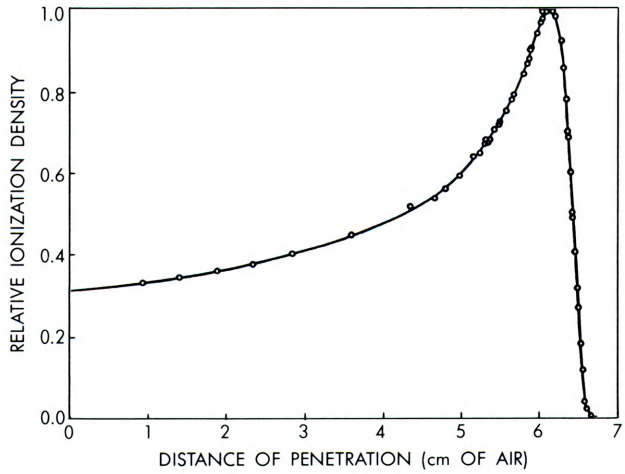


Figure 1. Variation of ionization density with penetration for a typical alpha particle.

cle, traverses matter, it "sees" mostly the negatively charged electrons, with which it strongly interacts. This interaction may produce merely electronic excitation in the interacting atom or molecule, or, at the other extreme, it may cause ionization, i.e., complete separation of the interacting electron from its parent atom. The energy of electronic excitation and ionization is supplied at the expense of the kinetic energy of the alpha particle, which therefore is continually slowing down. As its velocity decreases, the alpha particle remains longer in any one vicinity; hence, it interacts with increasing effect on vicinal orbital electrons, and the amount of ionization per unit of path length increases. After the particle has slowed down appreciably, it picks up two electrons to produce a neutral helium atom, and no further ionization occurs.

This behavior, which is characteristic of heavy charged particles, is depicted in Figure 1, in which the specific ionization (ions per unit of path length) is plotted versus distance traveled for a beam of monoenergetic alpha particles. It can be seen that the ionizing power of the alpha particle increases with penetration and then rapidly falls to zero. An immediate inference is that, aside from some statistical fluctuations termed straggling, monoenergetic alpha particles and other heavy charged particles will have a fairly well-defined range in a given material.

Another characteristic of heavy particle interactions is the essentially straight-line trajectory of the particle. Heavy particles are not readily deflected from their incident direction because of

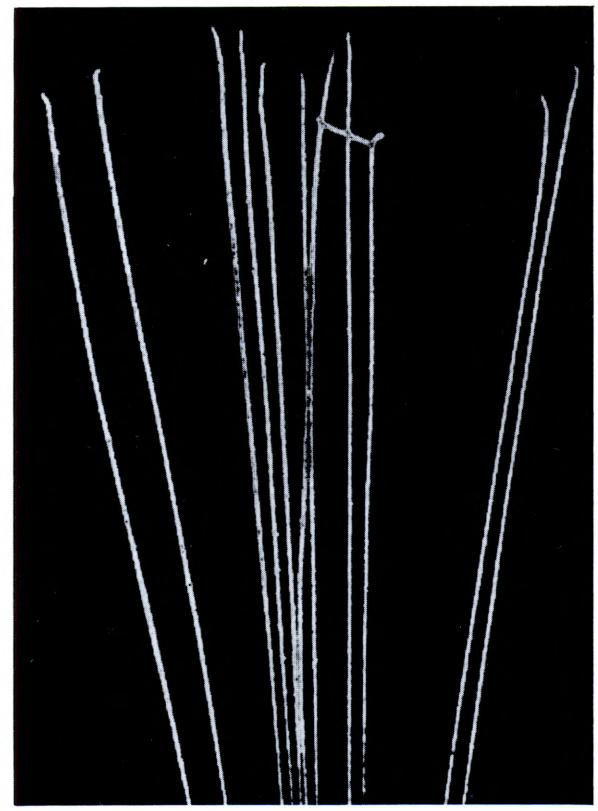


Figure 2. Illustration of "straggling" of alpha particles.

their high mass relative to that of the interacting electrons. Thus, for the most part, the excited molecules and ions produced by a given alpha particle will generally occupy a volume described by a right circular cylinder, frequently called the track of the alpha particle. This straight-line trajectory is shown in Figure 2, a cloud-chamber photograph of alpha particles. The fairly definite linear range of the particles is also evident in this photograph.

Omitted so far has been any discussion of the interaction between heavy, positively charged particles and atomic nuclei. Since the latter are also positively charged, the approach of a positively charged particle close to a nucleus is characterized by strong Coulombic forces of repulsion. Although it is possible to hurl an alpha particle into a nucleus and thereby produce a radioactive nucleus, the alpha particle must be accelerated to quite high velocities in order to acquire sufficient kinetic energy to overcome the potential energy barrier for the process. Until the energy of these positively charged particles reaches many million

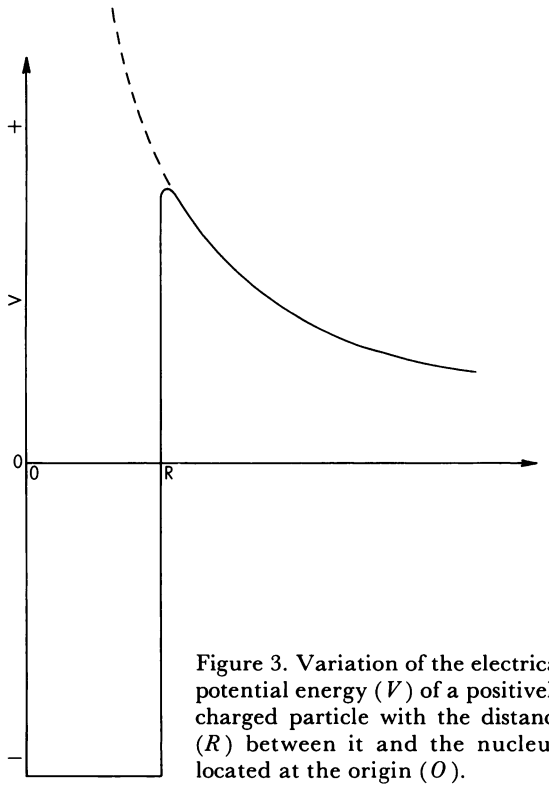


Figure 3. Variation of the electrical potential energy (V) of a positively charged particle with the distance (R) between it and the nucleus, located at the origin (O).

electron volts, direct nuclear interaction, leading to induced radioactivity, is improbable. The potential energy in the vicinity of a nucleus is shown schematically in Figure 3.

INTERACTIONS WITH BETA PARTICLES AND ACCELERATED ELECTRONS

Beta particles and electrons do not differ in essence from one another, but their origins are different. The former are electrons emitted from the nuclei of certain decaying radionuclides. There is much theoretical and experimental evidence to discount the possibility of the independent existence of an electron within the atomic nucleus. It is generally believed that the emitted beta particle is formed during the process of radioactive decay by the transformation of a nuclear neutron into a proton and an electron, the latter being expelled from the nucleus. Also involved in this process is the formation of a neutral particle of very small mass called a neutrino, about which more will be said later.

A beta particle has a charge of -1 and a mass only $1/1840$th that of a hydrogen atom or a proton. An electron of 1-Mev energy travels with a speed of 2.8×10^{10} cm/sec (94% the velocity of light in a vacuum) and has a range of $\approx$300 cm in air at standard temperature and pressure.

Electrons interact with matter in a fashion qualitatively similar to that for heavy, positively charged particles. That is, they cause electronic excitation and ionization by interaction with the orbital electrons of the absorbing medium. Because of their very light mass, however, they suffer more severe deflections during these interactions, and hence their trajectory is not a straight line. Moreover, an electron may lose a large fraction of its energy in a single collision with an orbital electron, with the result that straggling is much more marked in the case of electrons than in that of heavier particles. Electrons are also more readily scattered by atomic nuclei. Consequently, even though a beam of electrons is initially monoenergetic, the straggling and scattering make possible widely different path lengths for particles passing through the same thickness of absorber. The range of electrons in matter is thus a less precisely defined quantity than that for heavy charged particles.

Besides the loss of energy to an absorbing medium through electronic excitation and ionization, an additional mode of energy loss by fast-moving electrons must be taken into account: The ease with which the light electron is deflected in the field of an atomic nucleus causes deceleration, which leads to the emission of electromagnetic radiation by the charged particle at the expense of its kinetic energy. Denoting the energy lost per unit of path length due to this radiation by E_{rad} and that lost due to ionization by E_{ion}, the ratio of the two losses is given approximately by

$$E_{rad}/E_{ion} = TZ/800\,,$$

where T represents the kinetic energy of the electron in Mev, and Z is the atomic number of the nucleus. It is evident from this expression that the relative loss through radiation becomes more important as the energy of the electron increases and also as the atomic number of the absorber is increased.

The energy lost by this mode of interaction appears as a continuous x-ray spectrum called "bremsstrahlung" or "braking radiation." As will be discussed later, the penetration of x rays in matter is much greater than that of electrons with energies higher by orders of magnitude. For this reason, in shielding against highly energetic beta particles and especially electrons from very high

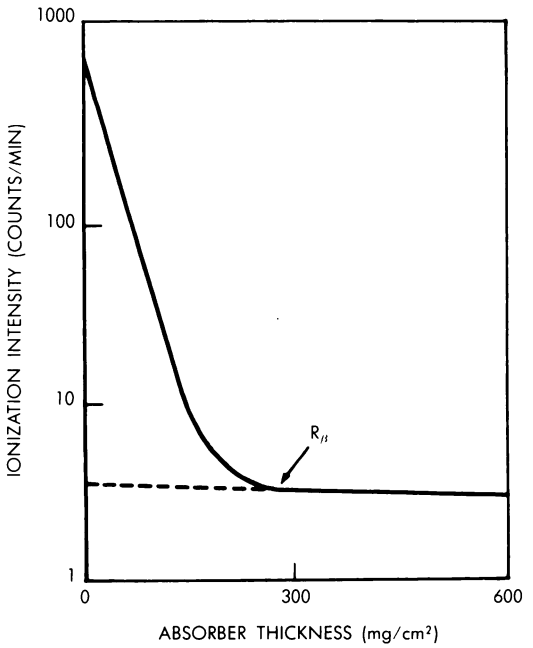


Figure 4. Variation of ionization intensity with absorber thickness for a continuous spectrum of beta particles.

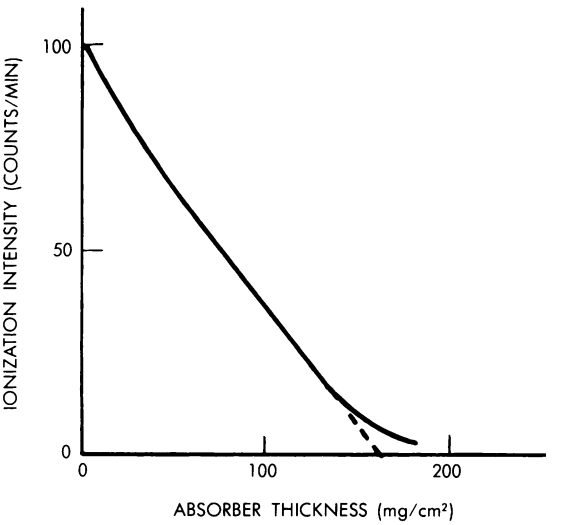


Figure 5. Variation of ionization intensity with absorber thickness for monoenergetic electrons having energy in excess of 0.2 Mev.

energy accelerators, the secondary x radiation is generally more of a problem than the primary electron beam, especially if the electrons impinge upon materials of high atomic number. Therefore it is advisable, when shielding against electrons, to use thicker pieces of a material of low atomic number rather than thinner pieces of materials of high atomic number. For example, a half inch of Lucite, if sufficient to stop the primary electrons, would be preferable to a few mils of lead, since the bremsstrahlung from the latter would present a much more serious problem than that from the former.

The beta particle, it will be recalled, is formed at the moment of radioactive decay by a process that can be summarized as follows:

$$\text{Neutron} \rightarrow \text{proton} + \text{beta particle} + \text{neutrino}\ .$$

The beta particle and the neutrino are expelled from the nucleus. Although both energy and momentum are conserved in the process, analytical mechanics predicts that in such a "three-body" situation the energy and momentum of each particle are not uniquely defined. In consequence, the beta particles emitted by a sample of a decaying material do not all have the same energy, but vary over a continuous spectrum up to some end point or maximum value corresponding to the total energy released by the decaying nucleus. Tabulations of beta-particle energies from beta-emitting nuclides are generally in terms of this end-point energy. As a very rough approximation, the average energy of the beta particles emitted by a nuclide is equal to one-third of the end-point energy.

This nonhomogeneity of the spectrum from a beta emitter, coupled with the severe straggling and scattering of beta particles in their passage through matter, gives rise to an exponential absorption curve for these radiations (Figure 4). The measured activity does not decrease to zero as the absorber becomes very thick but becomes practically constant at a value representing the so-called background. Near its end the absorption curve deviates from the exponential form, and the point at which it meets the background curve is called the range, R_β, of the beta particles. This is the distance traveled by the most energetic particles of the spectrum.

As indicated in Figure 4, thickness in absorption measurements is often given in units of grams (or milligrams) per square centimeter of absorber. The actual thickness is multiplied by the density of the absorber, and the resulting quantity, which may be called the superficial density, is used as a measure of thickness. It has been found that if the absorber thickness is measured in these units, the range is nearly independent of the nature of the absorber.

The absorption of monoenergetic electrons, e.g., those produced by an accelerator, is somewhat different. For electron energies in excess of 0.2 Mev the absorption is practically linear with thickness, as indicated in Figure 5. The linear portion of the curve can be extrapolated to intercept the thickness axis at a value called the extrapolated or effective range.

In calculating the amount of shielding needed for complete absorption of accelerated electrons or beta particles, recourse can be had to tabulated data and/or empirical formulas. The range-energy relationships refer to the maximum energy of the beta-particle spectrum or the energy of the monoenergetic electron beam.

The probability of inducing radioactivity by electron irradiations does not present a serious complication until energies of 5 to 10 Mev are reached. The electron does not directly react with the nucleus, but rather a secondary photon, emitted as a result of deflection of the electron in the nuclear field, can cause photodisintegration of the nucleus. However, with the advent of 20 to 30-Mev electron accelerators, induced activity from electron irradiations is becoming a problem for investigation.

INTERACTIONS WITH X RAYS AND GAMMA RAYS

As in the case of electrons and beta particles, the difference between x rays and gamma rays is essentially one of origin. Both are electromagnetic radiations. X rays are generally associated with the radiation emitted as a result of the transition of bound orbital electrons from higher to lower electronic energy levels; gamma rays arise in nuclear transitions from higher to lower nuclear energy levels. Since the latter energy levels are generally much more widely spaced than electronic energy levels, gamma rays are usually much more energetic than x rays.

Although an x or gamma ray is an electromagnetic wave it has an associated mass, given by Einstein's mass-energy relationship, $E=mc^2$. Thus, a 1-Mev gamma ray has an associated mass of approximately twice the electronic mass. The velocity of an x ray or a gamma ray is the same as that of light, and it is not possible to give a value of the range of this type of radiation, as will be more fully explained below.

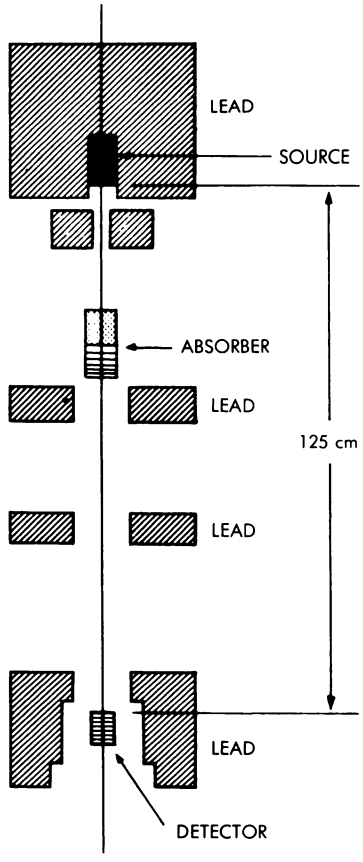


Figure 6. Schematic view of equipment for measuring total gamma-ray absorption.

As a beam of x rays or gamma rays passes through an absorber, a characteristic exponential decrease in the intensity of the radiation occurs. Thus, if the incident intensity is I_0, then the intensity I_x after transmission through a thickness x of absorber will be given by

$$I_x = I_0 e^{-\mu x} ,$$

where μ is the absorption coefficient. This relationship is true, however, only under certain well-defined circumstances, namely,

(1) the gamma rays are monoenergetic,
(2) the beam is collimated and of small angle, and
(3) the absorber is thin.

An experimental arrangement for studying the decrease in intensity of a gamma-ray beam under these conditions is shown in Figure 6. This arrangement provides a narrow, well-collimated beam. The thick lead shielding blocks act as the collimator. The counter used to detect the transmitted gamma rays is surrounded by lead shield-

ing to absorb any stray gamma rays and electrons arising from multiple scattering, and thus prevent their being counted. This whole arrangement is spoken of as a "good geometry" experiment because the photons are removed from the beam either by absorption or by a single scattering event. The decrease in the intensity of the beam in passing through the slab is a measure of the combined effect of these two processes. The experimental results of such an experiment are depicted in Figure 7, in which the exponential decrease in transmission of the photon beam is evident.

When x rays and gamma rays of the energies of interest interact with matter, three processes can occur, and the relative importance of each depends in a complicated fashion on the energy of the radiation and the atomic number of the absorber. The first of these processes, and the one of most importance at low energies, is photoelectric absorption. In this process, the gamma ray or x ray is totally absorbed, and in its place a high energy electron appears with a kinetic energy equal to the energy of the incident radiation minus the binding energy of the electron. The photoelectric effect is depicted in Figure 8(*a*). Below 50 kev (thousand electron volts) for aluminum and 500 kev for lead, the photoelectric effect is the main contribution to the absorption of x rays and gamma rays.

As the energy of the photon increases, another process replaces the photoelectric effect as the chief means of removing photons from the incident beam. In this process, known as Compton scattering [Figure 8(*b*)], an elastic collision occurs between the incident photon and an orbital electron. As a result, the photon is deflected from its initial direction; it also loses a fraction of its energy in producing a high energy electron through ionization. Both energy and momentum are conserved in this process. The change of direction of the photon serves to remove it from the initial beam. Thus, although only a fraction of the incident photon energy is actually absorbed by the ionization process, the entire energy of the photon is removed from the beam under the conditions of good geometry.

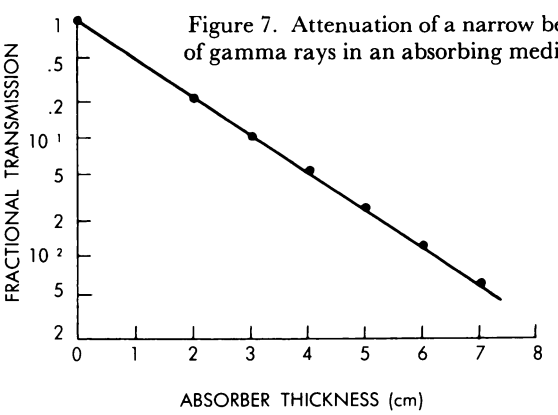


Figure 7. Attenuation of a narrow beam of gamma rays in an absorbing medium.

If the absorption coefficient obtained from such a narrow beam determination is employed in the calculation of the intensity from a broad beam at a great depth in the absorber, multiple scattering by the above process may yield experimental values that are many times greater than the calculated ones. The effect of such "build-up" from extended sources in extended absorbers has been experimentally determined in many cases, and empirical relationships to compensate for this effect in many specific instances have been developed.

Compton scattering gives the main contribution to the absorption of photons between 0.05 and 15 Mev in aluminum and between 0.5 and 5 Mev in lead.

At high enough energies, both the photoelectric effect and Compton scattering become unimportant compared with a third process, pair formation. In this process [Figure 8(*c*)], a photon in the Coulomb field of the nucleus disappears, and an electron and a positron are created. For pair production to occur, the energy of the incident photon must be at least equal to the energy-equivalent of the masses of the created electron-positron pair, i.e., 1.02 Mev. The total energy of the pair will then be equal to the energy of the photon in excess of 1.02 Mev. At photon energies greater than 5 Mev for lead and 15 Mev for aluminum, the probability of pair production is greater than that for Compton scattering and continues to increase with increasing energy.

In Figure 9 the individual contributions of the three absorption processes to absorption in lead, and the total absorption coefficient, μ, are shown as a function of photon energy. In Figure 10 the total absorption coefficient for photons as a function of photon energy is shown for absorbers of various atomic numbers. From these two sets of curves it is obvious that the absorption coefficient in any absorber shows a rather complicated dependence on photon energy, because of the interplay of the three absorption processes. It can also

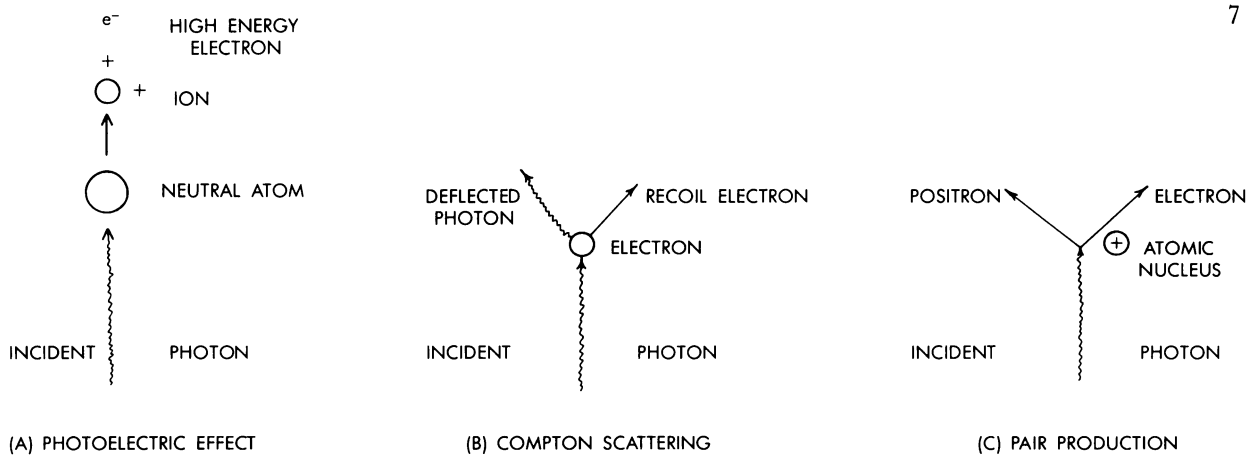


Figure 8. Schematic representations of three processes by which photons are absorbed in materials.

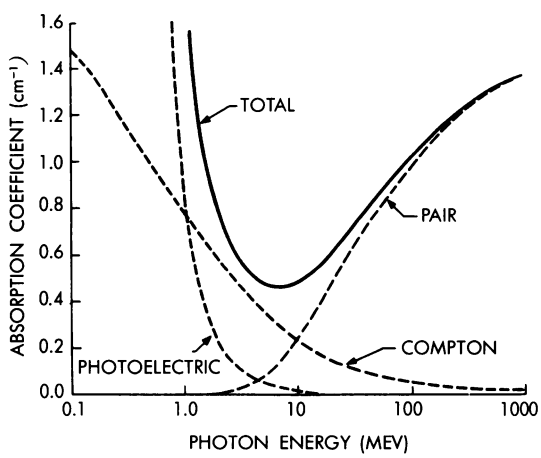


Figure 9. Total absorption coefficient of lead for photons as a function of energy, showing the contributions of photoelectric absorption, Compton scattering, and pair production.

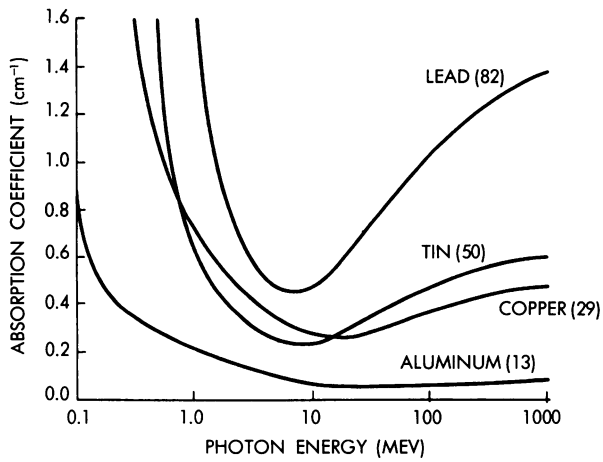


Figure 10. Total absorption coefficients for photons as a function of energy in several different metals.

be seen that the dependence of the absorption coefficient on atomic number is complicated.

Photons are also capable of interacting with nuclei. In this instance there is no electrostatic potential barrier to the process, since the photon is uncharged. The simplest type of photon-nucleus reaction is one in which the nucleus absorbs a gamma photon and emits a neutron. At low energies, neutron emission is more likely to occur than charged particle emission because, once again, no Coulombic barrier has to be overcome. One of the most common examples of this type of reaction, and the one requiring the least energetic photon, can occur in hydrogenous material, since the absorption of a photon in excess of 2.2 Mev by a deuterium nucleus will result in the emission of a neutron, which in a hydrogenous material will quickly be moderated to the range of energy in which neutron absorption by other nuclei becomes important. This latter reaction will be treated more fully below.

At present, the most widely employed source of gamma rays is Co^{60}, which emits two gamma rays of 1.17 and 1.33 Mev, neither one energetic enough to enter into the photodisintegration of any known nucleus. *Thus, the irradiation of any material by Co^{60} gamma rays cannot give rise to induced radioactivity.*

INTERACTIONS WITH NEUTRONS

A neutron is a nuclear particle that bears no electric charge and has a mass approximately the

same as that of a proton, or a hydrogen atom. Since the neutron is uncharged it is generally not capable of direct interaction with orbital electrons, in contrast to the radiations already discussed. Instead, neutrons generally interact with atomic nuclei.

Neutrons are produced only in nuclear reactions. Some nuclei spontaneously decay and in the process emit neutrons. Other nuclei, under proper stimulus, are induced to emit neutrons. The most intense source of neutrons available is a nuclear reactor. The operation of a reactor depends upon the fact that the nucleus of U^{235} (and a few other nuclei) will, upon the absorption of a neutron of very low energy (0.03 ev), fission into two unsymmetrical large fragments, with the emission of two or three high energy neutrons. These extra neutrons, after being slowed down (moderated), are then available for a repetition of the same process. Since for every neutron absorbed, more than one neutron is made available for the next step in the process, the reaction branches and can be made self-sustaining under proper conditions.

The neutrons present within the usual thermal reactor vary in energy from practically zero to 17 to 20 Mev. They are conveniently grouped into the following categories:

	Energy
Fast neutrons	>0.1 Mev
Intermediate neutrons	1 ev–0.1 Mev
Slow neutrons	<1 ev

Thermal neutrons are slow neutrons in thermal equilibrium with their surroundings; that is, they have essentially the same kinetic energy as the molecules of the medium in which they are traveling.

A so-called thermal reactor derives its name from the fact that the neutrons responsible for sustaining the fission chain reaction are thermal neutrons, which are derived from fast neutrons by proper moderation, discussed below. Other types of reactors are possible, but only thermal reactors are considered here because almost all reactors available for research work are of this type.

Neutrons undergo two main types of reactions with atomic nuclei: (1) absorption, in which a neutron enters the nucleus but other particles leave; and (2) scattering, in which the neutron interacts with and transfers a fraction of its energy to the nucleus, but remains free after the process.

The most common type of absorption reaction is radiative capture. In this process the nucleus absorbs the neutron, with the prompt emission of a capture gamma ray, and the resulting nucleus will generally be radioactive. The radiative capture process is generally more prevalent with slow neutrons than with more energetic neutrons.

There are two distinct types of scattering reactions undergone by neutrons, and their relative importance depends upon the energy of the neutron and the structure of the interacting nucleus. The type known as inelastic scattering is most probable for fast neutrons. For elements of moderate or high mass number, the neutron must have at least 0.1 Mev of energy, whereas even higher neutron energies are required for light nuclei. When a fast neutron undergoes inelastic scattering, it is first captured by the target nucleus; a neutron of lower energy is then emitted, and the target nucleus is left in an excited state. In other words, in an inelastic scattering collision a fraction of the neutron's kinetic energy is converted into excitation energy of the target nucleus and is subsequently emitted in the form of one or more photons of gamma radiation, called inelastic-scattering gamma rays.

Elastic scattering, the second type, is undergone by neutrons with energies below $\approx$0.1 Mev. In such a collision both energy and momentum are conserved. In each elastic collision with an essentially stationary nucleus, a neutron will transfer some or all of its kinetic energy to the target nucleus, depending on the geometry of the collision and the atomic number of the target nucleus. For example, in a head-on collision with a hydrogen nucleus (proton), the neutron can transfer all its energy to the proton. Thus, the occurrence of elastic scattering collisions in a hydrogenous material will produce fast-moving protons in the medium.

In addition, since it can transfer a large fraction of its energy in a collision with hydrogen (and other light nuclei), the neutron, after undergoing a series of such elastic scatterings, will be reduced to thermal energies. Reducing the kinetic energy of fast neutrons by scattering processes to produce low energy or thermal neutrons is the role of the moderator in a nuclear reactor; the process itself is called neutron moderation.

The probability of occurrence of any given neutron reaction is frequently given in terms of a quantity called the cross section for that reaction,

which is generally expressed in units of square centimeters. Many neutron reaction cross sections have a magnitude of the order of 10^{-24} cm^2, and this unit is called a barn. In both form and magnitude the barn appears to represent the actual cross sectional area of the nucleus. This concept is sometimes used to give geometrical significance to the barn. Some cross sections are as large as 10^5 barns and some as small as 10^{-5} barn, both obviously outside the magnitude of the geometrical cross section of any known nuclei; hence this picture of the cross section of a neutron reaction as analogous to the geometrical cross sectional area of the target nucleus is an erroneous, although useful, concept.

Another concept useful in the discussion of nuclear reactions is that of neutron flux. This is defined as the number of neutrons passing, per unit of time, through a unit of area oriented perpendicular to a unidirectional beam of neutrons. Therefore the unit of neutron flux is neutrons per square centimeter per second, in the metric system. If the neutrons are not unidirectional, the specification of the flux becomes more difficult. Another way of expressing the neutron flux is in terms of the product of the neutron density and the neutron velocity. In connection with nuclear reactors, it is customary to separate the total neutron flux into its various components and to speak of the thermal flux, the fast flux, etc. This is reasonable in view of the relative importance of various neutron reactions at different neutron energies.

In terms of neutron flux and cross section, the rate of a neutron reaction is given by the following expression:

$$R=\phi\sigma N=\phi\sigma\frac{WfN_{\text{Avog}}}{A},$$

where R is the rate (events per second), ϕ is the neutron flux, σ is the cross section for the particular reaction under investigation, N is the number of nuclei, W is the weight of the sample in grams, f is the weight fraction of the particular nuclide in the sample, A is the atomic mass of the nuclide in question, and N_{Avog} is Avogadro's number.

As an example, suppose that 100 grams of cobalt sulfate, $CO_2(SO_4)_3$, is irradiated in a thermal neutron flux of 10^{13} neutrons/cm^2-sec and it is desired to know the rate at which Co^{59} is transformed to Co^{60}. The cross section for thermal neutron activation of Co^{59} to Co^{60} is 36 barns. The rate of the activation can then be calculated as follows:

$$\text{Rate}=10^{13}\frac{\text{neutrons}}{\text{cm}^2\text{-sec}}\times 36\times 10^{-24}\,\text{cm}^2\times\frac{100\text{ g}}{59\text{ g/g-atom}}$$

$$\times 0.290\times 6.02\times 10^{23}\frac{\text{atoms}}{\text{g-atom}};$$

$$\text{Rate}=1.07\times 10^{14}\text{ atoms/sec}.$$

In the irradiation of any given material within a reactor, consideration must be given to at least two types of penetrating and damaging radiations – neutrons of all energies and gamma rays. The relative importance of the effects of these various radiations depends to a large extent on the relative neutron fluxes (of different energy ranges), the gamma-ray intensity, and the composition of the material being irradiated. A great deal of damage can be inflicted through elastic and inelastic scattering processes with fast and intermediate energy neutrons. The consequences of elastic scattering by hydrogen nuclei in organic materials have already been mentioned. This process leads to considerable internally generated proton irradiation. Similar effects can be produced in other materials containing elements of low atomic number.

The direct damage produced in the irradiated material by the radiative capture of neutrons in a sample is a less serious consequence than the radioactivity induced in the sample. It is practically impossible to place any material in a reactor without inducing radioactivity in the specimen because one or more of the main constituents of the specimen becomes activated, or, as frequently happens, the sample contains a small amount of an unsuspected impurity which has a high activation cross section. In fact, this latter source of induced radioactivity is a vexatious problem in reactor irradiations.

SUMMARY

Table 1, which represents an attempt to summarize and reduce many of the above concepts to more practical terms, contains a listing of some typical and representative irradiation sources and facilities. Columns 5 and 6 give an approximate idea of the efficiencies of energy absorption of the various radiations in a thin sample and a thick sample of a common material, polyethylene. Column 7 indicates the amount (and type) of shielding needed to protect personnel working in the vicinity of the various sources. These figures are based on an assumed exposure dose rate in air at

Table 1

Some Commonly Used Irradiation Sources and the Characteristics Associated With Their Radiations

Source	Particle or ray	Energy, Mev	Exposure dose rate in air, 10^6 rads/hr	Percent of incident energy absorbed in indicated thickness of polyethylene: 10 mils	1 in.	Amount and type of shielding to reduce exposure dose rate to normal background
Radioisotopes	Alpha	5	1	100	100	2 mils Al
	Beta	2	1	2.5	100	150 mils Al
	Gamma	1	1	0.16	10.5	10 in. Pb
Machines	Electron**	10	10^3	0.50	56	750 mils Al*
	X ray	0.050	5×10^2	0.55	42	50 mils Pb
Reactor	Gamma	1	1	0.16	10.5	5 ft concrete†
	Neutron**	up to 11 Mev	10^{13} thermal neutrons/ cm^2-sec	(0.3)	(26)	5 ft concrete†

*Does *not* include shielding against bremsstrahlung.
**May induce radioactivity in irradiated materials.
†Brookhaven Graphite Research Reactor "high-density" concrete.

the source as listed in column 4. It is obvious that shielding against alpha particles, beta rays, x rays, and accelerated electrons of moderate energy does not involve very large, bulky installations. Shielding against gamma rays and neutrons, however, requires the use of large, heavy shields, as does shielding against the bremsstrahlung associated with the use of very high energy electrons.

For those who may be interested in pursuing the question of the interaction of radiation with matter more thoroughly, the following references are given:

1. I. KAPLAN, *Nuclear Physics,* Chapters 2, 4, 13-16, 18-20, Addison-Wesley, Cambridge, Mass., 1955.
2. S. GLASSTONE, *Principles of Nuclear Reactor Engineering,* Chapter 2, Van Nostrand, Princeton, N. J., 1955.
3. H.F. JOHNS AND J.S. LAUGHLIN, Chapter 2 in *Radiation Dosimetry,* G. J. Hine and G.L. Brownell, Editors, Academic Press, New York, 1956.
4. S. GLASSTONE, *Sourcebook on Atomic Energy,* 2nd Edition, Van Nostrand, Princeton, N. J., 1958.

Part II

THE DETECTION AND MEASUREMENT OF HIGH ENERGY RADIATIONS

INTRODUCTION

The earliest recorded detection of high energy radiations is credited to A.H. Becquerel, who in 1896 discovered that crystals of a uranium salt emitted highly penetrating rays, capable of affecting a photographic plate through many layers of protective paper. Today use is made of this effect for the protection of personnel working with or near radioactive substances; these people wear film "badges" which register the amount of radiation to which they have been exposed. By covering part of the film with an extra shield of thick aluminum, it is even possible to differentiate between gamma and beta rays. The mode of interaction between these high energy radiations and the photographic emulsion appears to be the same as that between ordinary visible light quanta and the emulsion. The details of the latter process are as yet incompletely understood, but, broadly speaking, electronic excitations in the silver atoms of the emulsion are involved.

Becquerel discovered an even more useful effect of these emanations from radioactive nuclei: the induction of electrical conductivity in gases. This conductivity is caused by the formation of ions in the gas as a result of interaction with the radiation. This effect can be utilized both qualitatively and quantitatively to detect and measure high energy radiations. Most radiation detectors and dosimeters (devices used to measure the amount of energy deposited in a medium) depend on this ionizing effect of high energy radiations.

RADIATION DETECTION

Scintillators. Some materials, either in the pure state or impregnated with certain impurities (activators), luminesce when they interact with radiation. In these materials, both ionization and excitation lead to electronic energy transitions which, when reversed, are accompanied by the emission of visible light. Such materials are generally referred to as scintillators.

Zinc sulfide is one of the simplest and oldest scintillators. Its efficiency is greatly increased by including a trace amount of copper impurity. A detecting screen may be prepared by dusting a little of this powder on a thin glass sheet. Upon interacting with alpha particles the powder will luminesce in discrete spots, each spot indicating the absorption of an alpha particle. Since the efficiency of such a scintillator for gamma and beta rays is quite low, the zinc sulfide screen can be used to discriminate alpha particles from these two radiations. In addition, the number of alpha particles per second can be directly observed.

Not all scintillators release all their absorbed energy instantaneously; many exhibit the properties of photoluminescence or thermoluminescence. In general, such materials are regarded as storage phosphors. In the former class the residual energy, in the form of electrons trapped in metastable states within the crystal, can be released many hours after the absorption of the radiation by incident ultraviolet or visible light. The latter class is induced to emit its stored energy by application of thermal energy. If certain precautions are taken, the total fluorescent light emitted will be directly proportional to the radiation energy originally absorbed.

Scintillators for other types of radiation are also known. For instance, large single crystals of the alkali halides are the most efficient scintillators for detecting x rays and gamma rays. Certain organic crystals and solutions of organic materials in organic solvents are also used as scintillators. These organic scintillators generally have one characteristic in common – they contain in their molecular architecture an aromatic ring.

Electroscope. If the leaves of an electroscope are charged, as a rule the charge will slowly "leak" off the leaves. This is explained in terms of a low, but nonzero, concentration of charged gaseous particles in our surrounding atmosphere, the same particles that are considered to be the nuclei on which water droplets condense. Since radiations cause ionizations in gases leading to induced

conductivity, it is not surprising that a charged electroscope can be used as a radiation detector (Figure 1). The rate at which the charge leaks from the electroscope will be related to the amount of ionization caused by the radiation in the vicinity of the electroscope. Such an instrument is frequently employed, in a modified form, in conjunction with or in place of a film badge for personnel monitoring.

Ionization Chamber. To a certain extent, an ionization chamber is a continuous electroscope in which two oppositely charged electrodes are maintained at a constant potential difference by some external source of electrical potential. If an ion-pair (consisting of an ejected electron and the positively charged residue) is formed between these electrodes, each member of the pair will migrate toward the oppositely charged electrode and there become neutralized. If the current transported between the electrodes in this process can be detected and measured, the presence of radiation can be verified and its amount determined. However, since $\approx 6 \times 10^{12}$ electronic charges (ion-pairs) per second correspond to a current no greater than a microampere, it is obvious that if such a device is to serve as a detector, either a very intense source of radiation must be used or electronic amplification must be employed.

Figure 2 is a schematic diagram of an ionization chamber. The radiations ionize the gas between the electrodes and cause a current to flow. The ionization current causes a voltage drop across the resistor, R, which is detected and amplified electronically.

Ionization chambers can be used to count individual events, by recording the pulses of voltage caused by the collection of each ion-pair. If the ionizations occur too rapidly to be counted directly, an electronic device known as a scaler can be employed. The scaler can be set to signal a recording device after every 2nd, 4th, 8th, 16th, 32nd (etc.) individual event has occurred. Thus, the product of the reading on the recorder and the scale factor gives the total number of events that occurred in the chamber.

Without giving a detailed discussion of the physics and geometry of gaseous ion-recombinations and ion-collection, it will merely be noted that for most ionization chambers the voltage needed to assure collection of the maximum number of initially formed ion-pairs between the

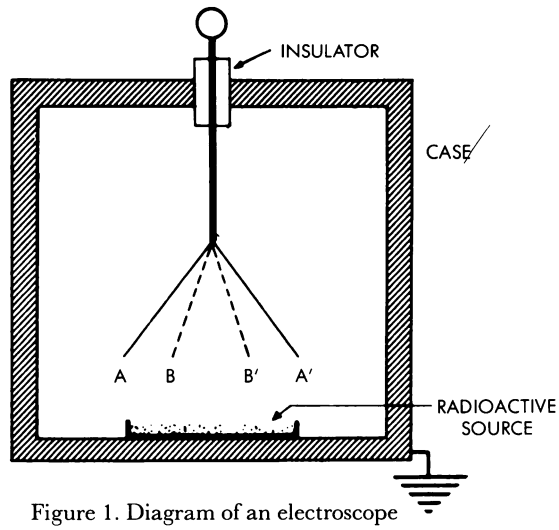


Figure 1. Diagram of an electroscope for detecting alpha particles.

electrodes is generally in the range of 40 to 250 volts.

Proportional Counters. If the voltage across the electrodes of an ionization chamber is increased above that needed to collect the maximum number of radiation-produced ions (the saturation current) a new phenomenon soon takes place. At higher accelerating voltages, the ions are greatly accelerated towards the oppositely charged electrodes, and some of them will acquire sufficient kinetic energy to collide with other gaseous molecules and ionize them. A "gas amplification factor" which increases with voltage is thus superimposed on the radiation-produced ionization. Under a given set of operating conditions of voltage and gas pressure, the amplification factor will be the same for each event, and the magnitude of the measured current or voltage pulse will be proportional to the initial ionization. An ionization chamber operating in this region is said to be a proportional counter. Under appropriate circumstances the pulse of ionization can be collected in a very short time. Gas amplification factors of 10^4 are commonly achieved.

The range of voltage over which an ionization chamber acts as a proportional counter is approximately between 250 and 600 volts.

Geiger-Müller Counter. If the voltage is increased even further, another interesting phenomenon occurs. The ions, both primary and secondary, are so greatly accelerated that, when they strike the electrode, electrons are emitted from the electrode and an avalanche of ionization spreads along it. This is especially true of the anode, to which the low mass electrons are accelerated.

Figure 3 is a diagram of a Geiger-Müller counter, with which gas amplifications of 10^8 or 10^9 are commonly attained. In Figure 3 the central electrode is the anode. As the highly accelerated electrons converge on it, a shower of electrons is momentarily ejected from the anode. These are recollected and measured as part of the pulse. The total amount of ionization is now determined by the type of gas, the voltage, physical dimensions, and other characteristics of the chamber, but is no longer dependent on the ionization produced by the primary particle. The range of voltage generally associated with a Geiger-Müller counter is 800 to 2000 volts.

Cloud and Bubble Chambers. Only a few words will be said about these devices, although for particle physics research they are extremely valuable tools. The former operates on the principle that ions act as nuclei for the condensation of supersaturated water vapor; the latter, on the principle that ions act as nuclei for vaporization of a superheated liquid, such as highly purified helium under pressure. Thus, if an ionization event occurs in the sensitive area of either device, its presence is visually observable as either a condensed droplet (fog) or a bubble. Further, the trajectory of the ionizing radiation is rendered visible by the locus of the vapor droplets or bubbles.

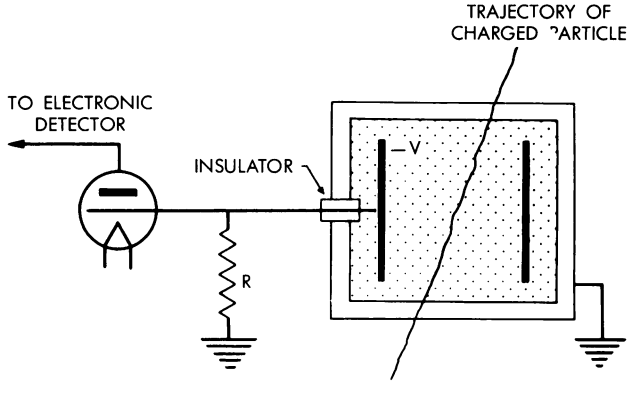


Figure 2. Ionization chamber for the detection of charged particles.

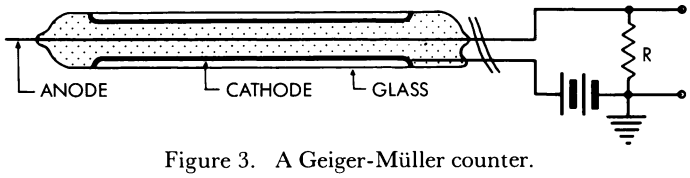


Figure 3. A Geiger-Müller counter.

All the radiation detectors discussed so far depend on the ability of the radiation to cause electronic excitation or ionization. Neutrons, however, are uncharged. As discussed in Part I, they interact mainly with atomic nuclei, rather than the extranuclear electrons. How, then, are they detected?

The detection of neutrons depends on secondary effects resulting from their interaction with nuclei. Some devices employing such secondary effects are discussed below.

Boron Counter. Neutrons are absorbed by the B^{10} isotope with the immediate release of an alpha particle. An ionization chamber or counter can be filled with BF_3 gas, or the walls may be lined with a boron compound. The incoming neutron releases an alpha particle from a B^{10} nucleus, and the alpha particle is detected by its ionization in the sensitive volume of the device. Since the cross section of the neutron capture process in boron is inversely proportional to the neutron energy, the boron counter is generally more suitable for counting and detecting neutrons of low energy.

Fission Counter. This device, which is capable of counting fast neutrons, slow neutrons, or both, employs a fissionable material such as uranium, in which either the 235 or the 238 isotope is enriched above the normal amount. U^{235} has the ability to undergo the fission reaction with either slow or fast neutrons, to produce fission fragments that are highly energetic, multiply charged particles, whose ionization density is even higher than that of protons or alpha particles. On the other hand, U^{238} can undergo the fission process only with fast neutrons, to give similar highly ionizing fission fragments.

It is possible to fill a counter tube with gaseous UF_6 or coat the walls with a uranium compound of such isotopic abundance as to respond to neutrons over the entire energy range. To detect fast neutrons, thorium, protactinium, and neptunium can also be used in this way.

Activation Counters. Many neutron-nucleus reactions lead to the formation of a radioactive isotope that will emit ionizing radiations. If an isotope with the proper combination of activation cross section, half-life of radioisotope, and energy of radiation emitted can be found, it can be used as a neutron detector. Many substances have been so used, among them indium, gold, manganese, and dysprosium. This method is also capable of

discriminating between neutrons of various energies, since the cross sections for activation are energy dependent.

Proton Recoil Counters. Since the masses of the neutron and the proton are essentially equal, the possibility exists that up to 100% of the kinetic energy of the incoming neutron will be transferred in an elastic collision between a neutron and a proton. The most common method of detecting fast neutrons is based on the observation of the ionization produced by fast recoiling protons in the elastic scattering of neutrons by hydrogenous materials. The counter used may be filled with a hydrogen-containing gas, or the window of the tube may be a solid hydrogenous material. The hydrogenous material may also be contained in a cloud chamber or in a nuclear emulsion.

UNITS AND DEFINITIONS

Up to this point, only the detection of radiation has been discussed. Before considering the more important subject of quantitatively determining the amount of energy deposited in a material as a result of interaction with radiation, it is advisable to define certain terms in common use. This is not an exhaustive glossary; it is intended merely to provide the basis for a general idea of the concepts involved. For a more complete knowledge of these quantities and concepts, recourse should be had to the references at the end of this section.

Curie. The amount of radioactivity in a sample is generally measured in a unit called a curie. One curie is defined as 3.7×10^{10} nuclear disintegrations per second.

Roentgen. Historically, the first unit of radiation energy dose was the roentgen, originally applied to x rays and subsequently modified to include gamma rays up to 3 Mev. The definition accepted by the International Commission on Radiological Units in 1953 is as follows:

> "The roentgen shall be the quantity of x- or γ-radiation such that the associated corpuscular emission per 0.001293 gm of air produces, in air, ions carrying 1 esu of quantity of electricity of either sign."

It should be noted that this unit depends solely on the ability of x and gamma rays to produce ionizations in air. The ratio of ionization to excitation will be reasonably constant in a given material, but it may change with changing atomic number. Thus, although it is a convenient unit for energy imparted to material of roughly the same average atomic number as air, the roentgen is difficult to apply to materials of arbitrary composition.

By definition, the roentgen is unsuitable for expressing radiation dose in the case of corpuscular radiations. Many units have been proposed from time to time to alleviate this difficulty, but most of them have fallen into disuse, are no longer recognized by the I.C.R.U., and will not be discussed here.

Rad. The rad is the unit of absorbed dose of any type of radiation. It is defined as 100 ergs absorbed per gram of material. Although it is not always possible to measure directly the energy deposited per unit mass, this unit is now widely used. Very careful measurements have established the absorbed dose in terms of an aqueous solution of ferrous ammonium sulfate, and x- and gamma-ray dosimetry of liquid and solid materials whose average atomic number and density do not vary much from that of water is usually carried out by this method and the results are expressed in rads.

Roentgen-equivalent-man (rem). This unit is intended to take into account the relative biological effectiveness (RBE) of different types of radiation. Although it is not officially listed as a unit by the I.C.R.U., its use is suggested when the absorbed doses of various radiations must be totaled. It is defined as follows:

$$\text{Dose in rem} = \text{dose in rads} \times \text{RBE} .$$

Table 1

Radiation	Biological effect	RBE
X rays, γ rays, and electrons, and β rays of all energies	Whole-body irradiation (blood-forming organs critical)	1.0
Fast neutrons and protons up to 10 Mev	Whole-body irradiation (cataract formation critical)	10
Naturally occurring α particles	Carcinogenesis	10
Heavy recoil nuclei	Cataract formation	20

Relative Biological Effectiveness (RBE). This term is intended to express the correlation between the various types of radiations and their effects on biological systems. Such factors, however, vary not only with the properties of the radiation but also with the biological effect studied. The I.C.R.U. has recommended the values of RBE shown in Table 1.

RADIATION MEASUREMENT

Ionization Chamber. The method of implementing the definition of the roentgen given above is illustrated in Figure 4, a schematic diagram of a parallel-plate ionization chamber. A narrow beam of x rays is shown passing between the parallel plates A and B. A collecting field of $\approx$50 to 100 volts/cm is applied between them, and the guard plates in electrode B define the field so that the collection of ions is restricted to the space immediately between the area C and the high voltage electrode, A. The separation of plates A and B must be sufficient to allow all the secondary electrons e_1, e_2, etc., to complete their tracks in air, and conditions of electron equilibrium must hold. The ions lost when an electron such as e_2 leaves the collecting space on one side are compensated by the corresponding part of another track, e_3, entering from the opposite side. The ions collected are then effectively those arising from x-ray absorption in the mass of air enclosed by the volume shown shaded in the figure, at a mean distance D_c from the source. Since attenuation of such a beam follows the inverse square law, this volume of air is equivalent to the smaller volume at D_s, given by the product of the area of the diaphragm, S, and the length of the collecting electrode, L. If the voltage change on the collecting electrode is V and the capacity of the measuring system is C esu, the dose in roentgens at the diaphragm is

$$\text{Dose} = \frac{CV}{300LS}\left(\frac{760}{p}\right)\left(\frac{273+t}{273}\right) \text{roentgens},$$

where the quantity in parentheses corrects for changes in air density under the conditions of measurement at temperature t° C and pressure p mm Hg.

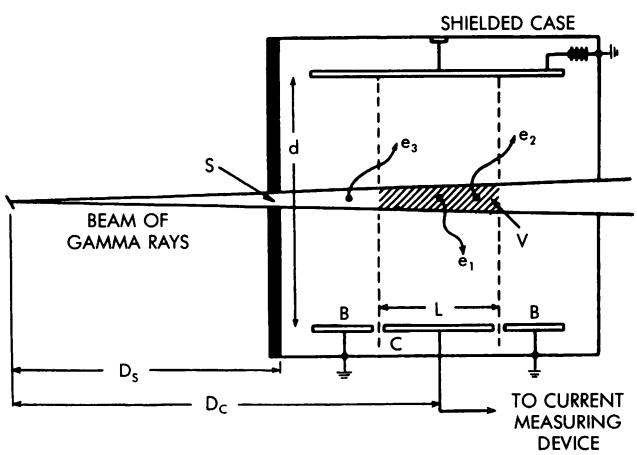


Figure 4. Diagram of an air-wall, parallel-plate ionization chamber.

In such an "air-wall" ionization chamber, the absorption of the primary radiation and the subsequent energy dissipation by the secondary electrons both take place in the same gaseous medium. Thus, a calculation of the true energy absorbed per unit of mass is limited chiefly by a knowledge of the amount of energy needed to produce one ion-pair in the gas. For a unidirectional beam of even reasonably energetic x rays, such an experimental method is easily adapted. What happens, though, if the incident radiation is not unidirectional? What happens when the radiations are as hard as 1-Mev gamma rays? If the highly penetrating radiation is or can be made unidirectional, the size of the ionization chamber could be increased to fulfill the requirements of electronic equilibrium. This has been done in cases in which radiations as high as 2 Mev were measured. The chamber, however, becomes quite large, in fact many meters in length and width.

It is much more convenient in such cases to employ a "thimble" ionization chamber. But here conditions are vastly different, since the walls of the chamber are irradiated and the ionization of the gas is due to electrons arising from absorption of the primary radiation in both the walls and the gas. It is not possible to construct the chamber's walls of a solid material having the same atomic composition as atmospheric air, although certain compositions can approximate the mass absorption coefficient of air. However, the electron-stopping powers and the energy spectra of the secondary electrons will not necessarily match those of air.

A relationship between the true primary energy absorption in the wall material and the ionization in the air or other gas filling the cavity of the

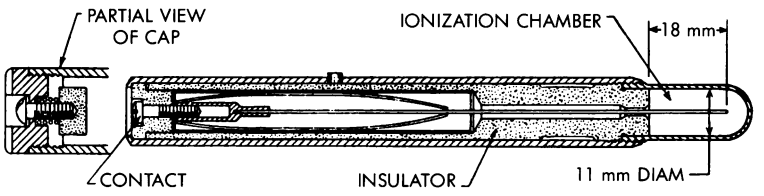


Figure 5. Details of construction of a Victoreen ionization chamber.

chamber may be derived if the size and geometry of the small ionization chamber meet certain basic conditions:

1. The cavity must be small enough so that only a very small fraction of the particle energy is dissipated in it.
2. Direct primary absorption by the gas in the cavity should be negligible.
3. The cavity must be surrounded by an "equilibrium thickness" of the solid medium.
4. The energy dissipation by the ionizing particles must be sensibly uniform over the volume immediately surrounding the cavity.

Under these conditions the Bragg-Gray theory[1] applies, and the ratio of the energy lost by an electron in traversing unit mass per square centimeter of medium to that lost per unit mass per square centimeter of gas is equal to the ratio of the mass-stopping powers of the medium and the gas. The energy imparted to the medium by the secondary electrons, E_m, can then be given by the following expression:

$$E_m = J_g \rho_m W ,$$

where J_g is the number of ion-pairs formed per unit mass of gas, ρ_m is the ratio of the electron-stopping power of the material to that of the gas, and W is the mean energy expended in the production of a pair of ions in the gas. Measurement of J_g and knowledge of ρ_m and W then determine the absorbed dose in the medium as set forth in the definition of the rad.

W might be expected to depend on the type of gas and the nature and energy of the ionizing particle. Although certain variations do occur, the value of W is remarkably constant over a large range of atomic composition of the gas, covering the range from pure argon and helium to atmospheric (dry) air, ethane, ethylene, and butane. It varies from 26 to 34 ev, except for electrons of very low energy, where its value rises to 41 ev for 0.3-kev electrons.

Calculation of the electron-stopping powers presents further difficulties. However, as the knowledge of collision processes and the required physical constants has increased, the accuracy of calculation has improved.

Victoreen Dosimeter. One of the most widely used ionization chambers of the thimble type is the Victoreen condenser dosimeter, which is shown in diagrammatic section in Figure 5. This dosimeter consists of an ionization chamber with an air volume of a few cubic centimeters mounted at one end of a shielded stem containing a solid dielectric storage condenser. Connection with the chamber is made through a contact at the opposite end of the stem, this being covered by a close-fitting cup when the chamber is in use. To charge the chamber or read its potential after irradiation, the cap is removed and the stem plugged into a socket on a metal box containing a quartz fiber electrometer, which is observed through a low-power microscope with an eyepiece scale to give a direct reading in roentgens. The walls of the chamber are made of Bakelite to approximate the absorption characteristics of air, so that the dose may be given in roentgens (r). Chambers of various capacities are available to cover the ranges 0 to 25 r, 0 to 100 r, and 0 to 250 r.

Most of the current work in the field known as radiation chemistry is being done by using gamma rays from Co^{60}, x rays, and accelerated electron beams from a Van de Graaff generator, resonant transformer, or similar electron accelerator. Various dosimetric methods for use in such devices have been developed, and some of those currently in use will be discussed here.

Faraday Cup. The transmitted electron beam from an accelerator can be measured by a device known as a Faraday cup, shown in schematic diagram (Figure 6). It is nothing more than an electron-collecting device in which the insulated collector is usually an aluminum block sufficiently thick to absorb the most energetic electrons. To

minimize the possibility of ion production by stray radiation the Faraday cup is generally mounted in an evacuated container, and aluminum is used to reduce the amount of bremsstrahlung and its associated secondary ionization. Since only the beam current is measured, the energy of the electrons must be known if the intensity of the beam is to be determined.

The Faraday cup cannot be used to measure the intensity at some point in a beam or radiation field, by virtue of its mode of operation. When connected in series with a transmission ionization chamber it can be used to calibrate the chamber.

Ionization chambers have been used to measure electron beam intensities, but various problems arise. Scattering of the electron beam and energy loss in the wall of the chamber represent serious shortcomings. The relatively large energy loss by electrons places a severe limitation on the thickness of the chamber walls to avoid serious perturbation of the beam energy.

The absorbed energy per unit of mass can be calculated from a knowledge of the intensity and initial spectrum of the electrons and the total collision-stopping power. The ratio of absorbed dose to cavity ionization density may be calculated for various wall materials, as in the case of an air cavity in a water medium. The resulting expression is quite complicated. In brief, the dosimetry of electron beams is a complicated matter on which there is as yet no universal agreement, especially with respect to the applicability of any one method to all the various electron generators.

Chemical Dosimetry. A more satisfactory state of affairs exists in the realm of hard x-ray and gamma-ray dosimetry for reasonably high doses and for the dose rates usually encountered with

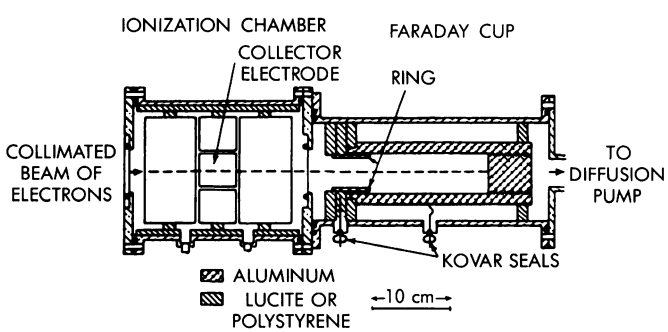


Figure 6. Diagram of a parallel-plate ionization chamber and a Faraday cup.

Co^{60} sources. The most widely used dosimeters in this area are chemical dosimeters, in which the absorbed dose is measured in terms of a chemical change in the dosimeter. Two such systems are the ferrous sulfate and the ceric sulfate dosimeters. The salient feature of both systems are summarized in Table 2.

The ferrous sulfate system has been thoroughly studied and widely accepted. The radiochemical yield of the ferrous dosimeter has been determined calorimetrically to be 15.6 ferric ions formed per 100 ev of energy absorbed. This dosimeter is generally accepted as a primary standard, and the radiochemical yields of other chemical dosimeters are usually determined by comparison with it. For instance, the yield in the ceric sulfate system is readily determined relative to that in the ferrous system; as indicated in Table 2, it is $\approx$6 times smaller than the value of the ferrous dosimeter.

The great practical value of the ferrous sulfate dosimeter (and most other chemical dosimeters) lies in the fact that the electron-stopping power of the solution and its density closely approximate those of materials of biological interest and also most liquid chemical systems. Unless systems with vastly different values of the above parameters are irradiated, it is the usual practice to equate the dose absorbed in the dosimeter with that absorbed in the material of interest.

Scintillation Dosimeters. Certain storage phosphors have been proposed as dosimeters. For instance, a silver-activated sodium chloride crystal 1 in. thick has a rather energy-independent response for gamma rays between 170 kev and 3 Mev. The phosphor can be stimulated to emit ultraviolet light of an intensity proportional to the total absorbed dose from 10^{-2} to 10^{4} rads. The crystal shows saturation and coloration after receiving doses of the order of 10^{5} rads, but can be restored by bleaching.

A great advantage of such storage phosphors is their smallness and relatively high sensitivity. They can be exposed in small light-tight and water-tight containers with no need for space-consuming equipment and can be measured later by means of a standard photomultiplier setup. A disadvantage is that the stimulated emission is in some cases quite dependent on the elapsed time between exposure and reading. For instance, the stimulated intensity of the silver-activated sodium chloride catalyst falls to $\approx$½ its initial value if 24 hr elapse before reading.

Table 2

Comparison of Ferrous Sulfate and Ceric Sulfate Dosimeters

	Ferrous sulfate	Ceric sulfate
Reagent	Ferrous ammonium sulfate	Ceric sulfate
Solvent	0.8 N H_2SO_4 in H_2O	0.8 N H_2SO_4 in H_2O
Reaction and yield	$Fe^{+2} \rightarrow Fe^{+3} + 1\ e$ (0.0164 μM Fe^{+3} per rad)	$Ce^{+4} + 1\ e \rightarrow Ce^{+3}$ (0.00273 μM Ce^{+3} per rad)
Range of independence of:		
Concentration	10^{-5} to 10^{-2} M Fe^{+2}	10^{-5} to 10^{-2} M Ce^{+4}
Energy of radiation	100 kev to 2 Mev	100 kev to 2 Mev
Dose rate	10^2 to 10^7 rads/hr	10^3 to 10^7 rads/hr
Total dose	0.2 to 4×10^4 rads (upper limit imposed by oxygen depletion)	0.2×10^4 to 1×10^6 rads (limit imposed by initial Ce^{+4} concentration)
Effect of temperature	Temperature affects only extinction coefficient of Fe^{+3}	Temperature affects only extinction coefficient of Ce^{+4}
Method of analysis	Spectrophotometric determination of Fe^{+3} formed	Spectrophotometric determination of Ce^{+4} remaining
Advantages	Large oxidation yield per unit absorbed dose; good for low level dosimetry	Small reduction yield per unit absorbed dose; good for high level dosimetry
		No back reaction
		Large change in optical density per unit change in concentration
Disadvantages	Back reaction at high Fe^{+2} concentrations	Extremely sensitive to trace organic impurities
	Autoxidation on long standing	

SUMMARY

The detection and measurement of high energy radiation depend almost entirely on the ionizations caused by the interaction of radiations (other than neutrons) with matter. Even in the case of neutron detection, a process of indirect ionization is employed. Some of the qualitative and quantitative aspects of this problem have been considered, but the discussion has not been exhaustive or even extensive. Many systems have not been mentioned; many of the details associated with the systems mentioned have not been fully explored. It is hoped, however, that some appreciation of the fundamental techniques has been conveyed. Those interested in pursuing this subject further are referred to

1. G.J. Hine and G.L. Brownell, Editors, *Radiation Dosimetry,* Academic Press, New York, 1956.
2. W.J. Price, *Nuclear Radiation Detection*, McGraw-Hill, New York, 1958.

Part III
RADIATION CHEMISTRY

INTRODUCTION

Certain formal resemblances exist between the well-established science of photochemistry and the more recent science of radiation chemistry. There are also marked differences between the two. It will prove valuable in the discussion of radiation chemistry to review briefly some of the fundamental aspects of photochemistry.

Photochemistry is the branch of chemistry that deals with chemical reactions resulting from the absorption of electromagnetic energy, usually from the visible or ultraviolet regions of the spectrum. The quanta of energy ordinarily involved in photochemical activations range from ≈ 1 to 5 electron volts (wavelengths between 10,000 and 2000 A, respectively). These quanta have sufficient energy to cause electronic excitation and bond rupture through vibrational excitation.

Since any molecule or atom activated by light absorbs only one quantum (Einstein's law), the number of molecules reacting will be equal to the number of energy quanta absorbed if, as a result of the primary absorption, only one molecule decomposes and the products enter into no further reaction. More frequently, however, a molecule activated photochemically initiates a sequence of thermal reactions as a result of which many reactant molecules may undergo chemical change. Furthermore, in processes where deactivation occurs, the net yield may be less than one molecule per quantum. The quantum yield (Φ) of a photochemical process is defined by

$$\Phi = \frac{\text{number of molecules reacting in a given time}}{\text{number of quanta of light absorbed in the same time}}, \quad (1)$$

which gives the number of molecules observed to undergo chemical transformation per quantum of absorbed energy.

The absorption of light quanta in this energy region is governed by quantum mechanical restrictions, the absorbed quantum corresponding to a discrete energy change in the atom or molecule. If the incident quantum has sufficient energy to excite an electronic and/or a vibrational mode, it may be wholly or partially absorbed and the absorbed energy will go into a specific excitation. Following the absorption process, a number of secondary processes may occur. The energy may remain concentrated in the mode (bond) and cause excited vibrations, perhaps leading to bond rupture. The energy may be redistributed throughout the absorbing system, giving rise to a number of less energetic vibrational and rotational states from which the molecule will frequently return to its ground state by collisional deactivation with other molecules in its surroundings. Finally, some or all of the energy may be reradiated as a quantum of equal or lesser energy.

If the re-emission is so rapid that it ceases when the exciting radiation is removed, the process is termed fluorescence. If the re-emission persists for some measurable time after the exciting radiation is removed, it is known as phosphorescence. Both processes can give rise to an interesting and useful phenomenon, that of indirect excitation. For instance, before it emits its energy an excited atom may collide with another atom or molecule, and in the collision part or all of its excitation energy may be passed along to the second particle, which thus is activated indirectly In some instances this indirect activation may lead to dissociation of the second molecule. This is termed photosensitization, and the first particle is referred to as the sensitizer.

With respect to the kinetics of photochemical reactions, the rate of the primary activating process is proportional to both the intensity of the absorbed radiation and the concentration of the absorbing species. The activation energy of the primary process is zero. This does not mean that the over-all activation energy of a photochemically initiated reaction will be zero, since, following the primary absorption, an activated molecule may dissociate into simpler molecules, or molecular fragments, which will propagate the reaction by thermally regulated steps.

Determination of the number of quanta absorbed in a system is readily made. The energy incident on the detector is measured both in the absence of the specimen and with the specimen between the source and the detector. The latter may be a thermopile, which converts the electromagnetic energy into heat and then into an electrical potential difference. Or, instead of a thermopile, a photoelectric cell may be used. A third alternative is to use a chemical actinometer, which is nothing more than a calibrated photochemical reaction. One of the more common actinometers is an acidified aqueous solution of uranyl acetate. Basically, in all these determinations, the absorbed energy is measured as the calculated difference between the observed incident intensity and the observed transmitted intensity.

GENERAL FEATURES OF RADIATION CHEMISTRY

Chemical activation can be obtained by the use of not only ultraviolet, visible, and near infrared light, but also alpha, beta, and gamma rays, protons, deuterons, and neutrons, all emitted by radioactive nuclei, as well as artificially accelerated electrons, protons, etc. The chemical reactions resulting from the interaction of systems with this family of radiations constitute the field of radiation chemistry.

In terms of energy these radiations cover a very broad spectrum, ranging from a few thousand electron volts (kev) to many millions of electron volts (Mev). The energy range usually considered is from a few kev to, perhaps arbitrarily, 50 Mev. Radiations of such extremely high energy can cause extensive changes when they interact with matter. With the exception of neutrons and charged particles having energies above 10 Mev, all these radiations interact with matter by two fundamental processes, electronic excitation and ionization, with the ejected electrons generally possessing sufficient kinetic energy to give rise to secondary, tertiary, and higher generations of excitations and ionizations. The fundamental aspects of these interactions have been covered in Parts I and II.

In a manner somewhat analogous to the photochemical quantum yield [Equation (1)], the radiochemical yield was originally expressed as

$$\frac{M}{N}=\frac{\text{number of molecules reacted or formed}}{\text{number of ion-pairs produced}}. \quad (2)$$

The denominator of this expression was easily measured as long as gaseous systems were the irradiated substrate. However, when the study of the radiation chemistry of condensed systems was undertaken, it became impractical to measure the number of ion-pairs produced by interaction with the radiation. The radiochemical yield was then redefined as

$$G=\frac{\text{number of molecules reacted or formed}}{\text{100 ergs absorbed}}, \quad (3)$$

and this is the most widely used measure of radiochemical yield today.

An approximate correlation between G and M/N can be obtained as follows. For most gaseous systems studied, the amount of energy deposited for the formation of one ion-pair lies in the range of 28 to 35 ev. If this same range is taken to be valid for condensed systems, then

$$G\approx 3(M/N). \quad (4)$$

Although photochemical reactions, governed as they are by quantum mechanical restrictions, are rather specific, this is generally not true of reactions initiated by high energy radiations. The latter involve energies so far in excess of any chemical bond or electronic energy level that the initial process is governed more by statistics than by quantum mechanical restrictions. The statistical nature of these reactions is exemplified by the experimentally observed fact that the ratio of methane gas to other products formed when saturated hydrocarbon compounds are irradiated is lower for straight-chain compounds than it is for branched-chain compounds, the reason being that the latter contain a higher percentage of terminal methyl groups.

Certain reactions, however, seem to be more specific and almost resemble photochemical reactions. For instance, in the irradiation of a series of straight-chain organic acids the yield of carbon dioxide is remarkably constant, despite the diminishing relative content of the —COOH group as the chain is lengthened. Again, a particular molecular grouping,

$$\begin{array}{c}-CH_2-C-CH_2-,\\ \quad\quad\|\\ \quad\quad CH_2\end{array}$$

is found in polyethylene only in a very small amount, but its rate of disappearance when polyethylene is irradiated is far in excess of what would be predicted on the basis of statistics.

Actually, the statistical nature of the process is more directly associated with the initial ionization event. The results of the various steps that then occur, especially the ultimate formation of stable products, are governed by molecular energetics, and hence may be quite specific. Yet, radiation-induced reactions are generally never as specific as photochemically induced reactions.

Phenomena similar to photochemical fluorescence, phosphorescence, and sensitization are exhibited in radiation chemistry. In fact, protecting a system against the damaging effects of radiation is frequently of greater interest than sensitizing a system towards radiation. The mechanism of protection is intimately related to that of sensitization. As an example, benzene is found to have a protective effect in the radiolysis of cyclohexane. One explanation is that the two structures have a series of interlacing energy levels and energy absorbed by the cyclohexane can be transferred to benzene. Because of the stability of the benzene molecule due to resonance, the energy thus transferred can be slowly degraded to heat without causing serious damage to the benzene structure.

On the other hand, sensitizers for radiation chemical reactions have been sought and studied. Some of the heavier rare gases, i.e., xenon and krypton, by virtue of their high electron density are good absorbers of radiation. In some instances it is possible to mix them with other gases that have lower ionization potentials and thus cause sensitization by charge transfer from the noble gas ion.

The kinetics of radiation-induced reactions are generally similar to those of reactions initiated photochemically. The activation energy of the initial interaction is zero, and the rate of the initial reaction is proportional to the intensity of the absorbed radiation.

The measurement of absorbed radiation dose has been discussed in Part II. It will be emphasized again, however, that, unlike photochemistry, in only a few special cases is it convenient to specify the amount of energy absorbed from a radiation field in terms of incident and transmitted intensities.

Figure 1 shows a broad range of the electromagnetic spectrum and some of the relationships discussed above.

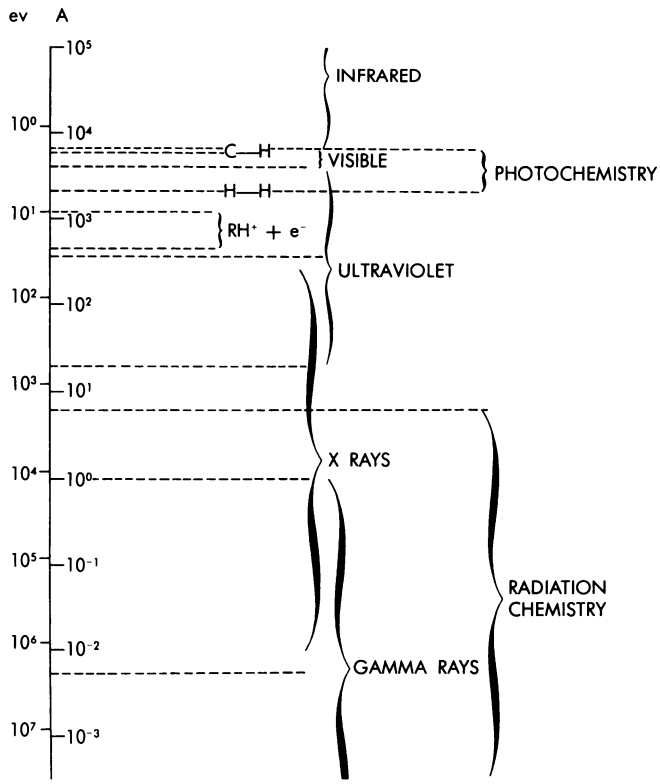


Figure 1. Part of the electromagnetic spectrum.

SOME DETAILS OF RADIATION CHEMISTRY

Of more specific interest are the types of chemical reactions that occur when matter interacts with high energy radiation. Quantitative differences can be expected in the effects of the various types of radiation, based principally on the density of ionization and hence the spatial distribution of the reactive species formed. Neglecting these effects, gamma-ray interactions will serve as a useful example of the qualitative aspects.

Gamma-ray interactions that transfer energy to orbital electrons usually do not cause extensive changes in materials such as metals and most crystalline, inorganic (ionically bonded) compounds, in which electron dislocations and rearrangements are frequently unstable. However, in substances for which the predominant mode of bonding is the sharing of electrons in covalent bonds, interaction with gamma rays gives rise to energy-rich molecular and atomic fragments that readily enter into various chemical reactions to form compounds not originally present.

What are these fragments and how are they formed? The ionization potentials of most covalently bonded compounds are in the range of 10 to 12 ev. If, after the initial ionization event, charge neutralization occurs by combination of a thermalized electron and a positive ion, the resulting uncharged molecule will have the same amount of energy (10 to 12 ev) to dissipate and will be an excited molecule. Since the energies of most covalent bonds are <4 ev, this charge neutralization energy is sufficient to cause bond rupture, yielding normal or excited fragments. This excitation process can also be achieved by direct interaction with the radiation.

A covalent bond may break in one of two ways. If the electron pair that constituted the original bond is divided so that each of the two separating fragments takes one electron with it, the process is called homolytic scission. Each of the fragments formed carries an unpaired electron, and each is a reactive neutral species. In the second mode of bond rupture, one of the separating fragments retains both the electrons that constituted the bond. Two electrically charged fragments result, an anion and a cation, and both may be highly reactive. This type of bond rupture is known as heterolytic scission. These two modes of bond rupture are shown below.

$$A{:}^{-}+B^{+} \xleftarrow{\text{heterolytic}} A{:}B \xrightarrow{\text{homolytic}} A\cdot+B\cdot$$

Ions — Free radicals

These reactions and processes that accompany and follow interaction with radiation can be summarized as follows:

$$AB+\gamma\rightarrow e^{-}(\text{high energy})+AB^{+}$$
(normal or excited ion),

$$AB+\gamma\rightarrow AB^{*}(\text{excited molecule}),$$

$$AB^{+}+e^{-}(\text{thermal})\rightarrow AB^{*}(\text{excited molecule}),$$

$$AB^{*}(\text{excited})\rightarrow A+B$$
(normal or excited free radicals),

$$AB^{*}(\text{excited})\rightarrow A^{-}+B^{+}(\text{normal or excited ions}).$$

Despite the fact that ions are formed both directly and indirectly in the above scheme, most reactions that have been studied, including those occurring in aqueous media where the dielectric constant is high, can be readily described in terms of free radical intermediates. Presumably the ions have such short lifetimes, especially in organic liquids of fairly low dielectric constant, that their effects are never noticed. Evidence is mounting that ion-propagated reactions may be more important in radiation chemistry than has been thought, especially under certain experimental conditions. However, the viewpoint adopted here will be that the predominant reactive species in the radiation chemistry of covalently bonded molecules are free radicals, under normal experimental conditions.

Two broad classes of compounds have been extensively studied: various substances in aqueous solution, and organic compounds in the pure state and in solution.

RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS

To simplify the explanation of radiation effects in aqueous solution, it is frequently assumed that the irradiation of water gives rise to H atoms and OH radicals, some of which instantaneously recombine to form H_2 and H_2O_2. Schematically, the interaction can be summarized as follows:

$$H_2O+\gamma\rightarrow H\cdot+\cdot OH+H_2+H_2O_2.$$

The many reactions that occur with solutes in aqueous solutions are then attributed to the oxidizing-reducing effects of H atoms, OH radicals, and H_2O_2.

As an example of the radiation chemistry of an aqueous solution, consider the chemistry of the ferrous sulfate dosimeter. It will be recalled that this system is an acidified, aerated aqueous solution of ferrous sulfate, in which the action of radiation is to cause oxidation of the ferrous ion to ferric ion. The reactions occurring are

$$H_2O+\gamma\rightarrow H\cdot+\cdot OH+H_2+H_2O_2,$$

$$H_2O_2+2Fe^{+2}+2H^{+}\rightarrow 2Fe^{+3}+2H_2O,$$

$$\cdot OH+Fe^{+2}+H^{+}\rightarrow Fe^{+3}+H_2O,$$

$$H\cdot+O_2\rightarrow HO_2\cdot,$$

$$HO_2\cdot+Fe^{+2}+H^{+}\rightarrow Fe^{+3}+H_2O_2.$$

The ferrous sulfate oxidation yield according to the above mechanism may be expressed as

$$G_{(Fe^{+3})}=G_{(OH)}+2G_{(H_2O_2)}+3G_{(H)}=G_{(-H_2O)}+3G_{(H)},$$

which is an example of the use of G values in expressing radiation yields.

It is apparent from the above description of the radiolysis of ferrous salt solutions in water that the incident radiation acts on the solute by an indirect process, the solvent participating in the initial ionizing event to form species that then react with any solutes present This is a fairly general phenomenon in the radiolysis of solutions. The same type of indirect action is encountered in many systems of biological and medical interest, especially those irradiated *in vivo*, since most living tissues are predominantly composed of water. Although a certain amount of direct interaction may occur, many workers in this field are inclined to believe that much of the radiation damage suffered in these systems occurs indirectly as a result of the strong oxidation-reduction potentialities of the H atoms and OH radicals formed in the direct radiolysis of water.

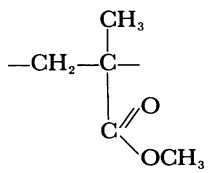
RADIATION CHEMISTRY OF ORGANIC COMPOUNDS

Returning to the radiation chemistry of organic systems, what are the reactions undergone by the radiation-generated free radicals? The nature and details of the various reactions that can occur depend to a great extent on the molecular structure of the material, its physical environment, and a number of other parameters. It will be convenient here to classify all the possibilities in three categories: (1) fragmentation, (2) polymerization, and (3) trapping of radicals.

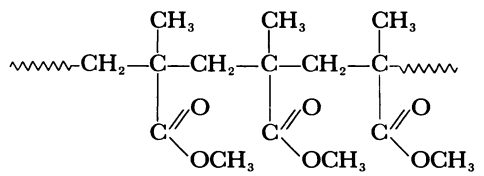
Fragmentation. When any hydrogenous material is irradiated, molecular hydrogen gas is inevitably one of the radiolysis products. If the irradiated material is a pure hydrocarbon, it follows that a certain number of carbon-hydrogen bonds are ruptured, to produce free hydrogen atoms. These, being mobile and reactive, can diffuse rapidly and abstract other hydrogen atoms to produce hydrogen gas. Strong evidence exists that, in addition to the hydrogen gas produced by free radicals, some fraction of the hydrogen is produced in what can be called a molecular reaction. In this type of reaction two hydrogen atoms on adjacent carbon atoms seem to be simultaneously expelled and immediately combine to form a hydrogen molecule. In either event, the formation of hydrogen gas in hydrocarbons results in double bond formation (unsaturation) in the parent molecule.

Other volatile fragments of low molecular weight are also formed through carbon-carbon bond rupture. To some extent, practically all the lower-molecular-weight products that can be formed by rearrangement of the various combinations of atoms in the parent molecule can be expected to result from radiolysis. However, not all of them lie within the range of analytical detection.

A rather dramatic demonstration of the fragmentation process can be seen in the case of irradiated poly(methyl methacrylate). The repeat unit in this material is

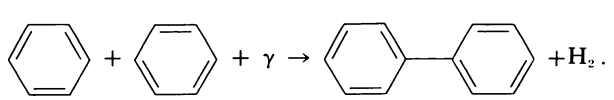


which leads to an idealized structure such as



If this polymer is irradiated at room temperature and then melted, the following gases are found in the radiolysis products: hydrogen, methane, carbon dioxide, carbon monoxide, oxygen, hydrocarbons other than methane, low-molecular-weight alcohols, and esters. The effect of this gas formation is strikingly evident in the physical appearance of the heated, irradiated polymer. Prior to heating, the radiolytically formed gases are trapped in the glassy structure of the polymer. Upon heating, not only do the gases expand but at the same time the glassy polymer is transformed to a more pliable liquid form. The internal bubble formation seen in the subsequently cooled specimen is graphic demonstration of the fragmentation process caused by the radiation (Figure 2).

Polymerization. The term polymerization is used here to denote a reaction that forms a product of higher molecular weight than that of the reactants. In this sense the formation of biphenyl when benzene is irradiated would be called polymerization. Schematically it can be represented by



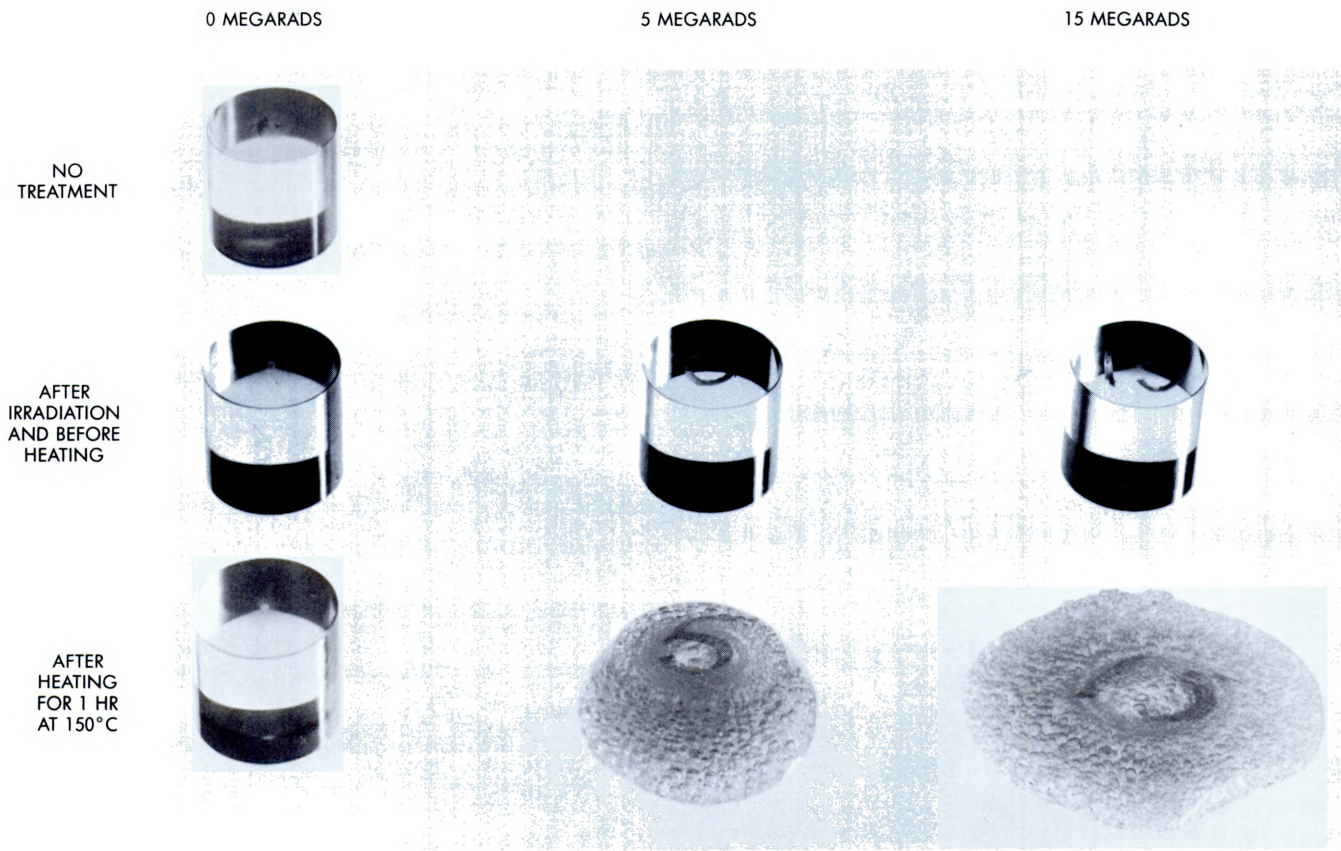


Figure 2. Fragmentation process in poly(methyl methacrylate). Note bubble formation and extreme deformation in irradiated samples after heating.

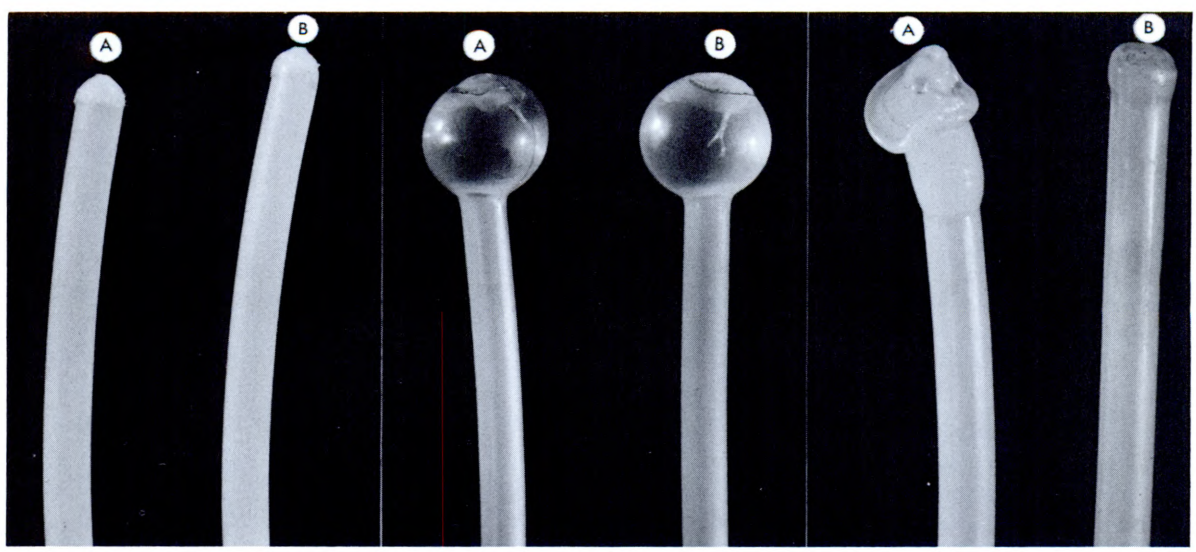


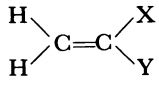
Figure 3. Effect of irradiation on mechanical properties of polyethylene. *A*, Unirradiated sample; *B*, sample irradiated with 30×10^6 rads. Note that irradiated material returns to its original shape.

The formation of glycols in the irradiation of alcohols,

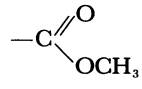
$$2RCH_2OH + \gamma \rightarrow \begin{matrix} RCHOH \\ | \\ RCHOH \end{matrix} + H_2,$$

might also be termed a polymerization.

A polymerization reaction of much greater proportions can occur if the irradiated material possesses a double bond which is at the end of the molecule. Such a molecule can be represented as



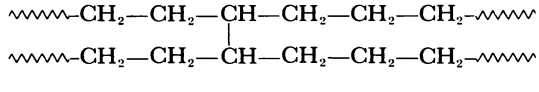
where X and Y may be hydrogen atoms, as in the case of ethylene gas, or one or both may be other than hydrogen groups. For instance, if X is $—CH_3$ and Y is



the molecule represents the repeat unit in poly(methyl methacrylate) described above.

When such molecules are irradiated, the polymerization reaction proceeds through opening of the double bond, and products of very high molecular weight are formed. The radiation-induced polymerization of these substances appears to proceed via the same kinetic route as that for conventional free radical polymerizations initiated by peroxides and photochemical sensitization. The products of radiation-induced polymerizations are not markedly different from those produced by more conventional means.

Another variety of polymerization that can occur under irradiation is the combination of two free radicals on neighboring chains to produce an intermolecular bridge, not really dissimilar from the first few cases of polymerization discussed. If, however, the original molecules are of polymeric proportions, the establishment of these intermolecular bridges effects marked and demonstrable changes in physical characteristics. For instance, two idealized polyethylene molecules can be pictured as undergoing this reaction, as follows:



If a sufficient number of these cross-links are formed, the softening point of the material is raised, its solubility in usual solvents may be entirely destroyed, and its mechanical properties such as tensile strength, elastic modulus, and stiffness can be greatly altered.

These changes in the properties of irradiated polyethylene can be readily demonstrated in a simple experiment. If a polyethylene tube sealed at one end is heated in hot glycerine and pressure is applied to the heated, semimolten, sealed end by blowing through the open end, a bubble is formed which will persist if the specimen is cooled to room temperature while maintaining the applied pressure. If this bubble is now replaced, without stress, in the hot glycerine, it will distort and flow. If, however, the polyethylene has been irradiated before this series of operations, the bubble will collapse when reinserted in the hot glycerine, and the polyethylene will regain its original tubular shape. (See Figure 3.)

The behavior of the irradiated material is ascribed to the intermolecular cross-links formed by the radiation, which cause the polyethylene to behave more like a vulcanized rubber than a plastic. When the heated bubble is allowed to cool under stress, crystallization of the polyethylene prevents the cross-links from returning the material to its original shape. Upon being reheated in the absence of applied stress, the crystallites melt and the cross-links return the sample to its original shape before crystallization can occur.

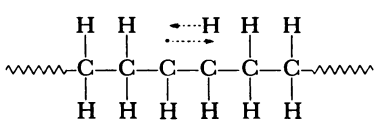
Trapping of Radicals. Of the three general processes discussed, the trapping of radicals is the most recently recognized. A radical may be considered to be trapped if its lifetime as a free species is extended by one or more orders of magnitude beyond the normally expected lifetime of a radical in a fluid system. The latter quantity is generally no greater than a fraction of a second. In a highly viscous liquid, or in an amorphous or crystalline solid, it is possible to form radicals having measured lifetimes of hours, weeks, and even months. These long-lived radicals are considered trapped. To understand how radicals can be trapped and thus "stored" in a system under certain conditions, a brief discussion of the mechanism by which radicals disappear is necessary.

The predominant mode of radical disappearance is through mutual reaction between two radicals. In a fluid system of low viscosity it is a simple matter for two radicals to approach each other by molecular diffusion and combine; each such reaction leads to the disappearance of two radicals

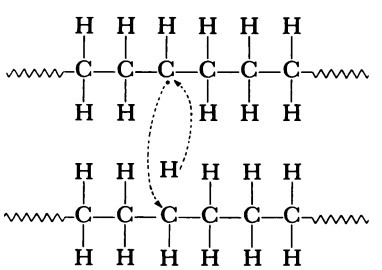
from the system. Anything that either reduces the mobility of the radicals or renders them less reactive because of inherent stabilization will increase their lifetimes.

In highly viscous liquids, and in amorphous or crystalline solids, the diffusion of all species is drastically reduced. The rate of radical decay under these conditions is greatly diminished, and hence radicals may become trapped. High-molecular-weight natural and synthetic polymers frequently exhibit the properties associated with a very viscous liquid, or an amorphous or crystalline solid, and are often capable of trapping free radicals for the reasons given above. In these high-molecular-weight systems, the radicals are also of very high molecular weight and have large size. The diffusion of such large species is hindered not only by the low fluidity of the medium but also by their inherent bulk.

To explain the cross-linking of such polymers by radiation, some mechanism must be assumed. Although the entire polymer chain, which may bear a radical somewhere along its length, may not be able to diffuse freely in the specimen, the segments of such a chain are in constant motion. If two segments each bearing a free radical manage to diffuse and achieve proximity, the two radicals may react, which results in their removal from the system and the formation of an intermolecular bridge. In addition, some investigators have postulated that a radical can migrate along a given chain



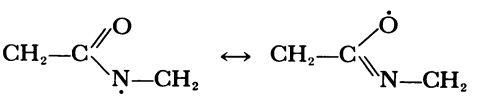
or from one chain to another



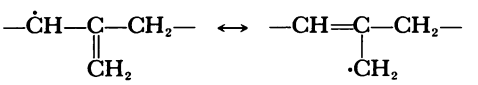
If such reactions occur, two radicals may achieve proximity not only by random segmental motion but also by migration along and across the chains independent of any chain motion.

Anything that will retard or inhibit either the segmental chain motion or the migration of radicals in high-molecular-weight polymers will increase the probability of formation of free radicals with appreciably long lifetimes. The former process is retarded by intermolecular cross-links, as in vulcanized rubber, or by any condition rendering the system more rigid, such as low temperature or crystalline regions in the polymer.

The process of radical migration, although less clearly understood, would probably be slowed down by the presence of sites along the chain at which the radical might be stabilized by additional resonance forms. In the case of nylon, the amide linkage would present two resonating radical forms, and if radical migration occurred along the nylon chain it might lead to an accumulation of the following types of structure:

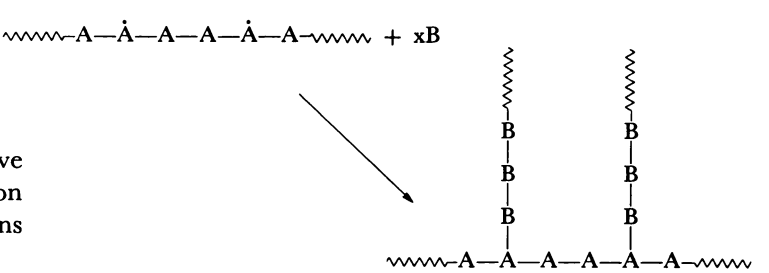


Some evidence for this type of radical migration exists in the previously mentioned rapid decrease in the pendant vinylene groups in irradiated polyethylene. When a radical reaches such a site the following resonance-stabilized forms can exist



Numerous examples of free radicals trapped in irradiated organic materials might be cited, but only two will be discussed here.

If polyethylene film is irradiated *in vacuo*, a small number of free radicals are trapped. These can be used, and their presence demonstrated, by contacting the irradiated film with a substance that can be polymerized by free radical catalysts. For instance, if *A* represents the ethylene unit of a polyethylene chain and *B* represents a second monomer species, such as styrene, the process can be represented by



TEMPERATURE (°C)	22	24	27	32	>200
TIME (MIN)	0	5	10	12	12+

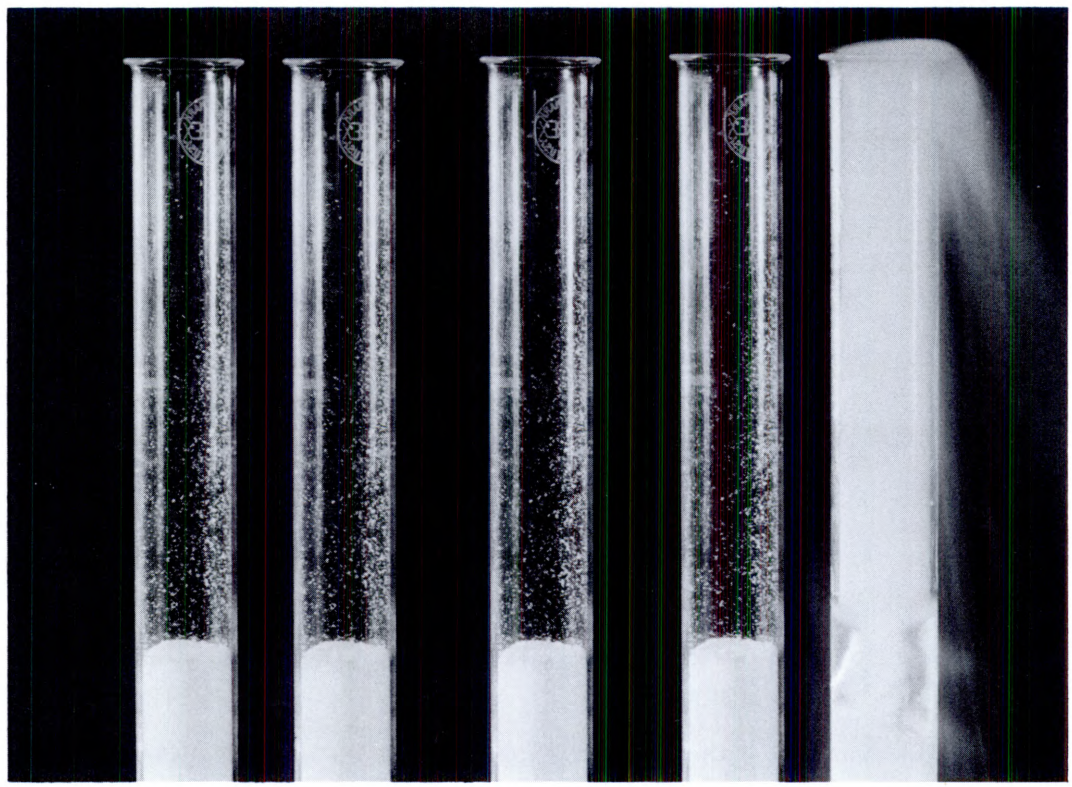
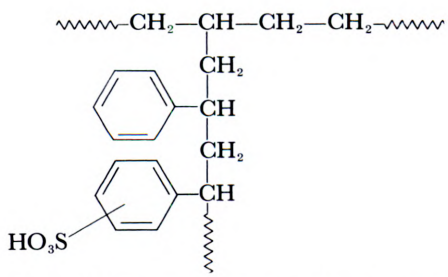


Figure 4. Release of trapped free radicals in acrylamide irradiated at dry ice temperature. Note fuming and fusion in last exposure of sequence.

The resulting featherlike structure is called a graft copolymer.

The graft copolymer between polyethylene films and styrene has been utilized as the starting point for the production of ion-exchange membranes. The graft copolymer is made by the above process, and then subjected to sulfonation, to produce the following structure:



where the sulfonic acid group is the ion-exchange site.

Another example of the trapping of free radicals is found in the case of irradiated acrylamide, a crystalline monomer that can be polymerized by free radicals to an amorphous polymer. Polymerization occurs during irradiation of this monomer at room temperature. Curiously enough, after the material has been removed from the radiation field, polymerization continues to occur, at a much reduced rate, for many months at room temperature. Measurement of the relative free radical content of the irradiated material as a function of time after irradiation shows that the rate of decay is very slow.

A high concentration of free radicals can be trapped in acrylamide if the irradiation is performed at a very low temperature, e.g., that of liquid nitrogen. At this temperature, the radicals formed do not have sufficient mobility to initiate the polymerization reaction, and hence are stored

in the system. If the irradiated sample is allowed to warm to room temperature, the radicals react and set off the following chain of events: polymerization, evolution of heat due to the polymerization reaction, heating of the sample to the melting point and beyond, and decomposition into volatile products, shown by the evolution of ammonia gas. Under some conditions of irradiation dose and geometry of the irradiated sample, the temperature may rise from room temperature to well over 200°C in a few seconds. Such a sample of irradiated acrylamide is shown in the act of "exploding" in Figure 4.

SUMMARY

The fragmentation and polymerization reactions discussed above occur in various ways and to varying extent in different organic molecules. Considerable work is being done in an attempt to understand the effect of molecular structure and state of aggregation on the distribution of the products of radiolysis, but broad generalizations are not yet possible. Perhaps the one generalization that can be made is that an aromatic group confers a remarkable degree of radiation stabilization on a molecule of which it is an integral part or with which it may be mixed in solution. The highly resonating benzene ring, with its inherent chemical stability, appears to act as an energy sink into which excess energy can be channeled and in which it can be slowly dissipated without causing extensive bond rupture. This has already been pointed out in the example of the protective action of benzene on cyclohexane.

The relatively high radiation resistance of other aromatic compounds, such as biphenyl and terphenyl, has proved advantageous in an experimental reactor in which a mixture of these compounds is employed as the moderator and heat transport medium. In addition, the use of anthracene and naphthalene as scintillators bespeaks the ability of these resonating systems to degrade some of the incident energy, in this case to the energy of visible light. The same type of radiation resistance appears to be present in polystyrene, a polymer in which every other carbon atom carries a benzene ring.

The salient feature of radiation chemistry is the nondiscriminating nature of the reactions that occur, which gives rise to a multitude of reactive molecular and atomic fragments. These then react and recombine to form products ranging from low-molecular-weight volatile gases to high-molecular-weight compounds in organic systems. In dilute solutions, the initial reactive species are generally those associated with the solvent. These fragments are capable of undergoing various reactions with the solute present, and thereby cause indirect radiolytic effects.

Many of the features of radiation chemistry are quite similar to those of photochemistry, the main differences being traced to the more specific character of the latter. Those interested in further details of radiation chemistry are referred, as a starting point, to the following works:

1. F. Collinson and A.J. Swallow, *Chem. Rev.* **56**, 471 (1956).
2. A.J. Swallow, *Radiation Chemistry of Organic Compounds*, Pergamon Press, New York, 1960.
3. A.O. Allen, *Radiation Chemistry of Water and Aqueous Solutions*, Van Nostrand, Princeton, N.J., 1961.
4. C.S. Lind, *Radiation Chemistry of Gases*, Reinhold, New York, 1961.